

CHEMICAL ABSTRACTS

Vol. 17.

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1—APPARATUS

C. G. DERICK

Improvements in the calorimeter bomb. G. BRUHNS. *Z. Zuckerind. czechoslovak. Rep.* 47, 479-81(1923).—A bomb of non-corrodible steel, which, because of poor proportions had a considerable lag, and of which the under side of the cover was badly attacked, has been improved by W. Cohen by putting 3 short legs under the bomb to improve circulation of H₂O, and putting a thin Pt shield over the crucible to prevent the flame from striking the under side of the cover. W. L. BADGER.

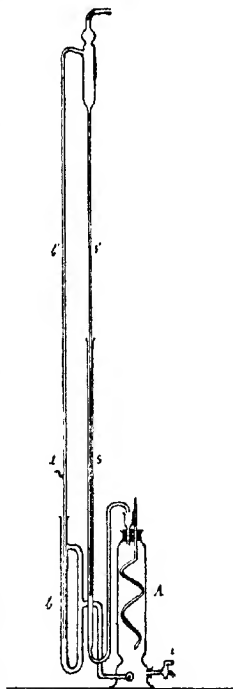
The recording ultramicrometer: its principles and application. J. J. DOWLING. *Phil. Mag.* 46, 81-101(1923). S. C. L.

Combustion boat with removable hood for the volumetric determination of carbon in the Mars furnace. G. PREUSS AND A. WOLFF. *Chem.-Ztg.* 47, 642(1923).—The porcelain boat is divided into 3 sections by 2 transverse ribs, each section being good for 1 C detn. A hood the length of a section is placed over the sample of Fe to protect the top of the combustion tube. J. H. M.

Load regulator for air and gas compressors. E. KRAHNEN. *Chem. App.* 10, 112-3(1923).—A cross-section of the app. is shown, and a cut showing it attached to a compressor. Cf. *Chem. App.* 1916, 106. J. H. MOORE

Bath temperatures of viscometers of the Saybolt type. W. H. HERSHEL. *Ind. Eng. Chem.* 15, 945-6(1923).—In using the Saybolt viscometer, standard bath temps. should be employed since the temp. of the outlet tube may be considerably different from the observed bath temp. Various factors affecting the temp. of the outlet tube are considered. E. C. BINGHAM

Apparatus for continuous extraction of solutions by means of nonmiscible solvents without the use of heat. M. JAVILLIER AND L. DESAINT-RAT. *Bull. soc. chim.* 33, 996-9(1923).—To ext. a compd. in aq. soln., the ordinary separatory funnel is generally used, but its use is restricted because the velocity of extn. is a function of the partition coeff., so that if this coeff. is small with respect to the second solvent, there is required a long time, an excess of solvent, and frequent renewal of the latter. The formation of emulsions is also undesirable. If extn. is made by distn. of the 2nd solvent which falls dropwise through the soln. to be extd. the difficulties encountered are: At temp. of extn., from acid or alk. solns, many org. compds. are easily decompd. and emulsification may occur. A new type of app. is presented, in which the circulation of solvent is accomplished, not by volatilization and condensation of solvent, but by aspiration with a water suction pump. An ordinary drying tower has 2 tubulatures at its base, one carrying a stopcock, the other a tube of shape *b* (see fig.). The stopper closing the top is fitted with a stirrer and a funnel tube. Into the top of the latter extends the vertical end of an S-shaped tube, with its other vertical arm open. A tall, inverted U-tube, 80



cm. in height, having at its upper end a reservoir and side arm for connecting to a water pump, is so placed that its 2 parallel arms, b' and S' , extend a short distance into the open ends of tubes b and S . A small open capillary is sealed into b' to admit air. The soln. to be extd. and solvent CHCl_3 are introduced into tower A . Being the denser, the CHCl_3 is at the bottom, and fills tube b to a certain height, depending on height of solvent in the tower and the density of the CHCl_3 . Tube S is filled with CHCl_3 just to the upper level in the small branch of b . Under gentle aspiration, the CHCl_3 rises in b' and air enters through the capillary k . A chain of bubbles of air and small columns of CHCl_3 rises in b' , reaches the reservoir, and descends through S' , again collecting in tube S , from which it drops through the funnel tube and into the soln. to be extd. Sinking to bottom of tower A , it rises anew, and repeats the performance automatically. It dissolves increasing amts. of substance until satd., as can be detd. by drawing a sample off through the stopcock. The advantages of the app. are: (1) When constructed of light tubing, it is resilient enough not to be easily broken in use; (2) loss of solvent by aeration is small, and solvents can be recovered by placing a Wolff bottle contg. cresol between app. and pump; (3) oxidation by the air is negligible. It is very satisfactory for extg. very unstable compds., estg. substances like saccharin in wine, and prep. very active Schweitzer's soln.

T. F. BUEHRER.
Radiator for platinum crucibles. M. M. GREEN. *Ind. Eng. Chem.* 15, 890(1923).

F. J. C.
A new observation tube for polarization. GUSTAV BLONCK. *Chem.-Ztg.* 47, 6642(1923).—If micro tubes (3 mm. diam.) for the investigation of protective enzymes in plants are made of dark glass a sharp field is obtained. The dark tube is surrounded by another tube and the space between is filled with H_2O at any desired temp.

J. H. MOORE.
A simple regenerative vacuum device and some of its applications. H. P. WARAN. *Proc. Phys. Soc. (London)* 35, 199-203(1923).—The accuracy and useful life of such vacuum devices as siphon gages and barometers are greatly increased by attaching to the closed end a small bent piece of capillary tubing terminating in a small bulb. Residual traces of air are forced through the capillary into this bulb at will by applying some pressure to the open end of the Hg column, and the Hg in the capillary traps the air in the bulb leaving a good vacuum in the space above the Hg in the gage, etc. This device is also used to prolong the life of certain types of Hg-vapor lamps.

C. C. VAN VOORHIS.
A stream-line filter. H. S. HELE SHAW. *Proc. Roy. Soc. (London)* 103A, 556-61 (1923).—Sheets of paper impervious to liquid are pierced with numerous large and small holes arranged in a suitable geometrical pattern, and embossed so as to form stream-lines from the large to the small holes. These sheets are assembled in packs of hundreds or thousands so that when they are pressed together the holes form tubes. End-plates are then so arranged that the large tubes are closed at one end and the small tubes at the other. The liquid to be filtered enters the large tubes under pressure and the filtrate escapes through the small tubes. The suspended matter remains in the large tubes until scraped out or flushed out by reversing the direction of flow. The filtrate passes from the large to the small tubes, not through the paper, but through the stream-line interstices, and since these may be made as small as desired by applying the proper pressure across the pack, it is possible to remove the coloring matter of what have been supposed to be complete sols such as aniline and other dyes. Also in *J. Soc. Chem. Ind.* 42, 353-67(1923).

C. C. VAN VOORHIS.
A device for water analysis and slow filtration. A. C. SIMMONS. *Ind. Eng. Chem.* 15, 901(1923).

E. J. C.
Quantitative Büchner filter. R. J. CROSS. *Ind. Eng. Chem.* 15, 910(1923).

E. J. C.
Plauson colloid mill. W. J. KELLY. *Ind. Eng. Chem.* 15, 926-28(1923).—A brief description of the Plauson mill presents theories of the action of the mill, and its industrial possibilities. Power consumption on motor-driven type is given as 4 to 5 watt-hrs. per lb. for emulsification of liquids.

A. E. MARSHALL.
Pumps for industrial purposes. F. W. TRAUDT. *Ind. Eng. Chem.* 15, 929-31 (1923).—Outlines fundamental conditions which govern selection of type of pump for industrial service.

A. E. MARSHALL.
Detector for water vapor in closed pipes. E. R. WEAVER AND P. G. LEDIG. *Ind. Eng. Chem.* 15, 931-4(1923).—A glass tube is coated with Pt and the coating divided by etching into 2 electrodes. Pt wires sealed through the glass connect the electrodes to a measuring circuit. The resistance to an alternating current of a thin film of a hygroscopic electrolyte bridging the gap between the electrodes is used as the measure

of the H_2O vapor in the atm. with which the film is in contact." The results are only approx. quant. The app. is shown in 3 cuts and the results in 3 charts. Cf. *C. A.* 14, 1278.

J. H. MOORE

Acetylene or other gas generators. H. KÜNTZEL. *Brit.* 192,456, Oct. 28, 1921. In generators in which the liquid (H_2O) in the liquid-storage chamber is maintained under pressure by the admission of an auxiliary pressure fluid such as O, the generation of gas is automatically regulated by means of a differential valve, which controls the supply of pressure fluid to the liquid-storage chamber, and which is itself controlled by opposing the pressure of the main supply of auxiliary fluid to that of the generated gas or to the pressure obtaining in the liquid-storage chamber. A suitable construction is specified.

Estimating impurities in gases. J. S. OWENS. *Brit.* 192,591, Jan. 20, 1922. An app. for use in estimating suspended impurities in air, etc., comprises means for causing a known vol. of air to strike a plate of glass or other material at such a high velocity that the suspended particles are caused to strike the plate and the moisture in the air is caused to condense on the particles prior to striking, and thereby cause the particles to adhere to the plate which is subsequently examd. under a microscope.

Apparatus for treating liquids with gases. D. G. ZALOCOSTAS. *Brit.* 192,393, Jan. 24, 1923. App. for treating liquids with gases comprises a tank with inlets for liquid and gas, gas outlet and liquid outlet and a tier of pairs of horizontal plates supported by jets and provided with a no. of down-turned nipples.

Apparatus for atomizing liquids. H. KERSHAW and H. CLARKE. *Brit.* 191,775, Aug. 20, 1921. App. for atomizing liquids for disinfecting, humidifying, liquid-fuel burning, and other purposes, of the kind in which the supply or delivery of liquid only takes place when the pressure of air or other atomizing fluid exceeds a predetd. amt., is so arranged that when the atomization is arrested, free and uninterrupted passages are open so that all unatomized liquid is drained away, such drainage being assisted by air suction.

Apparatus for feeding sulfur dioxide in liquid or gaseous condition or for feeding other materials. C. W. HOTTMANN. U. S. 1,463,818, Aug. 7. The app. is adapted for supplying SO_2 to tanks for rendering animal or vegetable fats or oils.

Device for supplying oxygen. P. HEYLANDT. U. S. 1,464,319, Aug. 7. Liquid O is contained in a double-walled flask with the space between the walls evacuated and liquid is conducted out of the inner vessel and around its neck through a coil situated in the evacuated space around the neck.

Evaporating apparatus. E. G. WILLIAMS. U. S. 1,464,793, Aug. 14. Solns. of H_2SO_4 , sugar, salt, tannin or other liquid to be concd. are heated in a shallow vat by combustion gases which pass first beneath and then over the vat. Agitating devices throw some of the liquid up into the current of combustion gases to facilitate the evapm.

Apparatus for controlling temperatures of chemical reactions. C. R. DOWNS and C. G. SRUPP. U. S. 1,464,845, Aug. 14. The app. is adapted for exothermic vapor-phase reactions, *e. g.*, partial oxidations of C_6H_6 , $C_{10}H_8$, toluene, phenanthrene, $PhNH_2$, *o*-cresol, $PhOH$, xylene, $MeOH$, $EtOH$, aliphatic hydrocarbons, NH_3 or SO_2 or for chlorinations of other reactions in which close temp. control should be observed. Cooling pipes or other cooling devices are placed on each of 2 opposite sides of supports carrying a catalyst for the reaction, out of direct contact with the catalyst, so as to abstract heat generated by the reaction, by radiation from the catalyst and its support to the cooling devices. The reaction chamber is preferably enclosed in a flue heated to about the desired reaction temp.

Heat-exchanging apparatus adapted for use as a condenser in refrigerating systems. J. C. GOOSMANN. U. S. 1,464,705, Aug. 14.

Heat regenerators. H. J. F. PHILIPON. U. S. 1,464,580, Aug. 14. Fused quartz in the form of tubes with thin walls is used as the medium through which heat interchange takes place.

Producing vacuums for heat insulation. J. H. DELANY. U. S. 1,464,698, Aug. 14. Condensation of vaporized Zn or other gas or vapor is utilized as the sole means of creating a vacuum in the jackets of glass heat-insulating devices.

Roasting furnaces. D. BAIRD. *Can.* 233,139, July 31, 1923.

Filter presses of the plate and frame type. L. D. MILLS. *Can.* 233,552, Aug. 14, 1923.

2-GENERAL AND PHYSICAL CHEMISTRY

GEORGE L. CLARK

The series of discoveries by Pasteur. PASTEUR VALLERY-RADOT. *Rev. sci.* 61, 417-24(1923). Pasteur and general chemistry. CHARLES MOURRU. *Ibid* 425. Pasteur and the fermentation industries. A. FERNBACH. *Ibid* 426-31. Pasteur and hospital hygiene. LOUIS MARTIN. *Ibid* 432-6. Pasteur and rabies. JULES GUIART. *Ibid* 437-8. Pasteur and exotic pathology. F. MRSNIL. *Ibid* 439-42. Pasteur and surgery. H. VINCENT. *Ibid* 443-6. Pasteur and maternity. PINARD. *Ibid* 447-51. The works of Pasteur and hygiene. D. DE LA RIVIÈRE. *Ibid* 452-8. Pasteur and sericulture. PAUL MARCHAL. *Ibid* 459-64. Pasteur and agriculture. HENRI HITIER. *Ibid* 465-7. Pasteur and veterinary medicine. E. LECLAINCHER. *Ibid* 468-71. Pasteur and urbanism. C. P. HEIL. *Ibid* 472-5. E. J. C.

The discovery of aluminium by Oersted in 1825. I. FOGH. *Kgl. Danske Videnskab. Selskab. Math. fys. Medd.* 3, No. 14, 17 pp.(1921).—An historical paper relating to Oersted's expts. which led to his discovery of Al previous to its isolation by Wöhler.

L. T. FAIRHALL

Russian chemical biography for 1917 and for 1918. Compiled by B. N. MENSHUTKIN. *J. Russ. Phys. Chem. Soc.* 51, II, Nos. 1-2, 1-22(1920).—This well classified bibliography contains all available chem. references to articles in periodicals (except the *J. Russ. Phys. Chem. Soc.*), pamphlets and books. W. A. PERLZWEIG

Edward Hart. E. C. BINGHAM. *Ind. Eng. Chem.* 15, 974-5(1923).—A brief biography, with portrait. E. J. C.

J. Willard Gibbs and his contribution to chemistry. F. H. GETMAN. *Science* 18, 120-33(1923). E. J. C.

Obituary of Dr. Christian Hess. C. DUISBERG. *Z. angew. Chem.* 36, 413-4 (1923); portrait. E. J. C.

The importance of the physics of incommensurable particles in physical investigations. ERWIN FREUNDLICH. *Naturwissenschaften* 11, 399-402(1923).—A comparison of the methods employed in investigations in physics and astronomy with a discussion of the development of the theory of relativity and its relation to the electron. C. C. DAVIS

The conception of valence. E. A. SUILOV. *Ber. Polytechnikum Ivanovo-Wosnissensk* 6, 417-21; *Chem. Zentr.* 1922, III, 206.—From a discussion of the valence theory of Kekulé, of that of Werner and of the electrostatic theory, it is concluded that no theory is completely satisfactory. The structure of the mol. is dependent upon various phys. causes and for this reason it is considered impossible to formulate a universal valence theory. C. C. DAVIS

The rare earths in the periodic system. CARL RENZ. *Z. anorg. allgem. Chem.* 122, 135-45(1922).—A general consideration of the peculiar position in periodic tables to which the rare earths have been assigned. C. C. DAVIS

The element boron. A. H. WARTH. *Bull. Maryland Acad. Sci.* 3, No. 3, 8-9 (1923).—A new method for the prepn. of relatively pure B consists in the reaction of BCl₃ with H in the presence of a glowing W filament at 1300-1850°. The B deposits on the W, from which it is easily stripped. It is harder than sapphire, and brittle; it has a high tensile strength. The sp. resistance is 9×10^6 ohms per cm.² at 26°. This drops in half for 12-17° increase in temp. The d. is 2.3; the coeff. of expansion is approx. 2.0. G. L. CLARK

Preparation of pure BCl₃ and BBr₃ for atomic weight determination of boron. ALFRED STOCK and ERNST KUSS. *Ber.* 56B, 1463-6(1923).—The prepn. and purification of the materials for the at. wt. detn. of Höngschmid and Birckenbach (*C. A.* 17, 2524) is described. Three lots of BCl₃ were purified; 40 cc. previously prepd. from Moissan B and Cl₂ and used for detn. of phys. consts.; a new sample of 30 cc. similarly prepd.; 50 cc. of com. BCl₃. After removal of Cl₂ by Hg and distn. the only impurities present were HCl and SiCl₄. These were removed by repeated fractional distn. and condensation in the vacuum app. with control by tension measurements at 0°. On account of the widely differing b. p. (HCl, -85°; BCl₃, 12.5°; SiCl₄, 57°) sepn. is fairly rapid. All the final samples showed 477 mm. at 0°. These were sealed into small glass bulbs. Details of precautions to exclude moisture, etc., in this operation are given in full. BBr₃ was prepd. from B (Moissan) and at. wt. Br₂, furnished by Höngschmid. Purification was by the same methods used for BCl₃. After the fifth fractionation the 0° tension, 18 mm., was const. After 5 further fractionations the material was sepd. by slow distn. into 15 fractions and the m. ps. of fractions 1, 2 and 15 were measured

with the NH_2 -tension thermometer. All melted sharply at -46° (NH_2 -tension, 387 mm.). This pure prepn. was sealed into 7 bulbs.

Study of carbon. PELAYO POCH. *Anales soc. españ. fis. quim.* 21, 291-304(1923).—The finely divided C obtained by decomposing pure CN by the elec. spark was submitted to an X-ray examn. and found to contain cryst. particles. The allotropic forms of C are discussed at length.

Structural units of starch determined by X-ray crystal structure method. O. L. SPONSLER. *J. Gen. Physiol.* 5, 757-76(1923).—A regular arrangement of the planes of starch atoms is indicated by the lines of X-ray spectrum negatives. These lines agree with the lines that would be produced by a lattice of the tetragonal system; the elementary cell of this system is a square prism, $5.94 \times 5.94 \times 5.05 \text{ \AA}$. This cell occupies a space equal to the vol. of the starch group, $\text{C}_6\text{H}_{10}\text{O}_5$. A model of the starch group was constructed which fulfils the requirements necessary to produce the reflections obtained with starch. The starch grain is built up of units arranged in concentric layers; these units are atomic groups, each contg. 6 C, 10 H and 5 O atoms. The structure is neither amorphous nor cryst. as commonly understood. Cellulose also consists of a regular arrangement of $\text{C}_6\text{H}_{10}\text{O}_5$ groups, but with a spacing of $6.14 \times 6.14 \times 5.55 \text{ \AA}$. The $\text{C}_6\text{H}_{10}\text{O}_5$ starch group is probably the starch mol. A clear picture of the starch units and their arrangement will give a new point of attack on problems of osmosis, swelling and polarized light. Methods are described. Cf. also *C. A.* 17, 1822.

Molecular and crystal symmetry. T. V. BARKER. *Nature* 112, 96(1923); cf. *C. A.* 17, 2375.—Rejoinder to Shearer and Astbury (*C. A.* 17, 2525).

Symmetry of calcium thiosulfate hexahydrate. W. T. ASTBURY. *Nature* 112, 53-4(1923).— $\text{CaS}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$, usually quoted as the unique example of the triclinic asym. crystallographic class (C_1), would be expected to have a space lattice with only 1 mol. per unit cell if "Shearer's rules" continue to have no contradictions (*C. A.* 17, 1741). However, the X-ray results are in full agreement with a 2-mol. cell. While nature, in variance with her usual procedure, might have used an asym. polymer of the chem. mol., yet it is much more likely that $\text{CaS}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ really belongs instead to the pinacoidal class C_2^1 , for the following reasons: (1) in all complex crystals so far examd. the ultimate structural unit has proved to correspond to the chem. mol.; and (2) there is a mass of evidence to show that crystal symmetry, as deduced from a study of facial development and etched figures, is often of lower type than the true structural symmetry as deduced from X-ray data (e. g., NH_4Cl). The inference is that the 2 mols. of $\text{CaS}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ are inversions of each other, as in the cases of racemic acid, anhydrous and mono-hydrate, and hence that the structure is centro-sym.

A crystallization phenomenon. C. R. BAILEY. *Nature* 112, 10(1923).—Photograph and description of salicylic acid crystals suspended in the soln. by practically invisible threads below the surface layer.

Molten salts. II. W. HERZ. *Z. Elektrochem.* 29, 274-6(1923); cf. *C. A.* 16, 4117.—The internal pressures in atmospheres and the mol. diam. in cm. $\times 10^{-4}$, resp., of molten alkali halides are: LiF 59,800, 0.23; LiCl 21,300, 0.40; NaF 38,800, 0.32; NaCl 18,900, 0.36; NaI 11,200, 0.44; KF 23,500, 0.35; KCl 13,600, 0.38; KBr 11,300, —; KI 8510, —; RbF 17,800, 0.46; RbCl 12,400, 0.32; RbBr 9940, 0.44; RbI 7650, 0.49; CsF 13,400, 0.53; CsCl 10,200, 0.31; CsBr 8070, 0.56; CsI 8550, 0.43. The product of the modulus of expansion and the abs. b. p. of molten alkali halides is approx. const.

Relations between the contraction of chemical compounds and their other properties. J. J. SASLAVSKII. *Ber. Polytechnikum Iwanowo-Wosniessensk* No. 6, 407-12; *Chem. Zentr.* 1922, III, 214-5.—It has already been shown (cf. *Ber. Polytechnikum Iwanowo-Wosniessensk* No. 1) that the vol. of stable compds. is 0.5 as great as the vols. of their elementary components (normal contractions). This is not true of acids and bases, for acids show a smaller and bases a greater contraction than the normal. With these compds. a relation exists between the elec. cond. K and the contraction C . In acids C increases with K ; in bases the opposite occurs. Sulfides, arsenides and alloys show a very small contraction. In solns. which form no hydrates, the contraction curve changes uniformly with change in contraction, but with formation of hydrates the contraction curves show breaks so that a means is at hand for detg. the existence of hydrate formation.

Sulfuric anhydride, a chemical chameleon. M. LE BLANC AND C. RÜHL. *Ber. Verhandl. Säch. Akad. Wiss. Leipzig* 74, 106-44(1922).—In the study of the photochemical reaction of SO_2 and O_2 at 150° and at pressures of a few tenths of an atm., const. results could not be obtained when attempts were made to condense the SO_3 formed.

Knietsch reported (1901) that liquid SO_2 has a vapor pressure of 0.4 atm. at 35° , but earlier writers claimed that several modifications exist. B. and R. therefore studied the vapor pressure of SO_2 at varying temps., and found that at all temps between 0° and 20° almost any vapor pressure from 20 to 195 mm. could be obtained at will. By using appropriate condensation conditions it was shown that 4 groups of values were represented, corresponding to 4 modifications with m. ps. as follows: *a* between 95 and 100° , *b* at about 31° , *c* at 16.8° , and *d* probably at a still lower temp. For varieties *a*, *b* and *c* vapor d. detns. indicate a formula SO_2 . It was very striking that the modification *d* was formed when the variety *c* solidified at 16.8° after supercooling; a spontaneous, almost explosive, elevation of the vapor pressure took place. W. C. E.

Kinetic theory of heat conductivity, viscosity and diffusion in certain condensed gases and liquids. D. ENSKOG. *Svensk Vetenskapsakad. Handl.* 63, No. 4, 44 pp. (1922); *Physik. Ber.* 3, 1274(1922).—The above theory is based on the assumptions that mols. are hard, smooth, perfectly elastic spheres, and that the distribution of the velocities is Maxwellian. Special assumptions as to the law of force are made. Results are compared with expl. data, and the deviations discussed. A. E. STERN

The compressibility of gases at 0° and at less than one atmosphere and the deviation from Avogadro's law. T. BATUECAS. *Anales soc. españ. fis. quim.* 20, 441-58 (1922).—Very pure gases were maintained at 0° in glass bulbs and the vols. measured at various pressures between 230 and 840 mm. The calcd. values of the deviation from Avogadro's law, expressed as $1 + \lambda$, are: O_2 , 1.00085; H_2 , 0.99935; CO_2 , 1.00706; C_2H_6 , 1.0078; N_2O , 1.00739; NO , 1.00112; Me_2O , 1.0254. Cf. C. A. 16, 3249.

Free paths in a non-uniform rarefied gas with an application to the escape of molecules from isothermal atmospheres. J. E. JONES. *Trans. Cambridge Phil. Soc.* 22, No. 28, 535-56(1923).—Mathematical. In the most recent treatment of the problem of the rate of dissipation of an atmosphere by Milne, the method involved the neglect of all collisions beyond an arbitrary height which was virtually regarded as the ceiling of the atm. It also involved the use of a formula which is shown to be valid only in a gas of uniform *d*. This is not satisfactory, for at the height at which it is applied the free paths of the mols. must be so enormous that there is a sensible change of *d* along a free path. With no assumption about mol. velocities except their distribution according to the Maxwellian law, general formulas have been derived for free paths in a non-uniform rarefied gas where the free path is a function not only of its velocity but also of its origin and direction of motion. For a mol. to escape from an atm., it must have its last collision above a certain crit. height and must subsequently move within a certain "cone of escape" appropriate to the point of collision. The dissipation has been calcd. not by the usual formula for the no. of mols. of specified velocities crossing a plane, which is not applicable when the gas is rarefied and non-uniform, but by considering the collisions in each element of vol. of the upper atm. and enumerating those which result in one of the mols. having a velocity of such magnitude and direction as to satisfy all the conditions for escape. The rate of loss is proportional to the first or second power of the basic mol. concn. according as the crit. level is free or fixed. The loss of He from Mars is considered in some detail. A. E. STERN

Escape of molecules from an atmosphere, with special reference to the boundary of a gaseous star. E. A. MILNE. *Trans. Cambridge Phil. Soc.* 22, No. 26, 483-517 (1923).—Mathematical. The escape of mols. from the fringe of a gaseous, gravitating atmosphere in which the temp. falls off as the *n*th power of the distance from the center of the nucleus is investigated with the help of the concept of the "free solid angle" at any given level. On Eddington's theory of the internal equilibrium of a star, out of all possible masses, the masses of the existing stars are grouped about that which has the least gravitational potential at the surface in the giant stage. In spite of this the loss is found to be completely negligible for all stars. In considering the escape of electrons from the surface of a star, it is shown, in agreement with other writers, that the potential of the sun must be positive when in a steady state; and that it cannot permanently exceed 1900 volts or be less than 30 volts. The potential of a giant M star should be between 15 and 44 volts. A. E. STERN

Preliminary experimental confirmation of the two-film theory of gas absorption. W. G. WHITMAN. *Chem. Met. Eng.* 29, 146-8(1923).—All later theories for the phenomenon of gas absorption assume that the absorption rate, dW/dt , is proportional to the product of a driving potential factor and operating and construction coeffs. The driving potential varies as the distance from equil. In the two-film theory (cf. C. A. 10, 2785; 16, 1354) it is held to be the difference between the partial pressures of the solute in the gas and in the liquid. In the other and opposed case (cf. C. A. 14,

2971; 15, 715, 2137; 17, 2463) it is given as the difference between the concn. of the solute in the gas and liquid. Both expressions give results identical at const. temp. with a solute obeying Henry's law. The controlling factor in the rate of absorption is the rate of diffusion through the surface films between the gas and liquid. W holds that diffusion occurs through a gas film and is caused by the partial pressure difference of the solute in the gas and that in equil. with the liquid in the film. Opposed to this is the theory that the diffusion occurs through a liquid film on the liquid surface and is due to a difference in concn. between the solute in the gas and in the liquid. Work done on humidification (cf. *C. A.* 16, 1354) shows that the rate of diffusion is controlled by the gas film around the liquid and the liquid film on the liquid. The degree of importance varies with the conditions. The diffusion through the gas film is detd. by the partial pressure gradient of the solute ($p_1 - p_2$) and through the liquid film by the concn. gradient ($c_1 - c_2$) thus: $dW/d\theta = k_p(p_1 - p_2) = k_l(c_1 - c_2)$, where W is the amt. of gas absorbed, θ the time of absorption, k_p the coeff. of absorption through the gas film and k_l that through the liquid film. The last 2 coeffs. depend on the exptl. conditions. The two equations, $dW/d\theta = K_p(p_1 - p_2)$ and $dW/d\theta = K_l(c_1 - c_2)$, where K is an over-all coeff., apply only to cases where the concn. varies as the pressure and Henry's law holds. In the case of HCl and water, the partial pressure of HCl is small and can be neglected up to about 250 g. per l. but rises rapidly above this point. Hence with surface concns. below this, gas will be absorbed at rates depending on the rate of diffusion through the gas film, while with higher acid concns., the equil. pressure is high and varies rapidly with the concn. Hence a few exptl. data are used to confirm this theory.

P. D. V. MANNING

A differential form of the equation of state at higher pressures. VICTOR FISCHER. *Ann. Physik* 69, 315-24(1922).—F. defines the quantity b , analogous to the " b " in van der Waals' equation, by means of the expression $T(\partial v/\partial T)_p = v - b$ for H_2O vapor, Et_2O , and N. The value of v is const. to 3% for changes of temp. of 40°. The ratio of the crit. vol. to b varies from 3.6 to 4.1, instead of equalling 3.0, as it does in the equation of van der Waals. At abs. zero $(\partial v/\partial T)_p$ must equal zero. This case is considered theoretically.

F. R. BICHOWSKY

Analytical study of vaporization. M. DAMIENS. *Ann. chim.* 19, 179-85(1923).—A study of the vaporization of solid mixts. indicates the existence of compts. in the gaseous state. The vaporization of solid mixts. was studied by heating the mixt. ground and sieved to uniform fineness, in sealed and evacuated tubes, the lower ends of which were placed in an electrically heated Al block. The sublimate collecting in the upper part of the tube was analyzed. In this manner it was shown that in the systems $TeCl_4-Te$, $TeBr_4-Te$, and TeI_4-Te , there existed an equil. of the type: $TeBr_4 + Te \rightleftharpoons 2TeBr_2$.

T. S. CARSWELL

The gas-impelling forces originating on the surfaces of contact of dissimilar porous substances. I. I. KOSSONOGOV. *Ber. Polytech. Iwanowo-Wosniessensk* 6, 57-71; *Chem. Zentr.* 1922, III, 326.—Expts. show that a movement of gas at the surfaces of contact of dissimilar porous substances is caused by gas-impelling forces. The strength of the gas current depends upon the nature of the porous substances and in the expts. it was a few tenths of a mm. with a water manometer.

C. C. DAVIS

The movement of gases through porous bodies. K. M. KOSSONOGOV AND I. I. KOSSONOGOV. *Ber. Polytech. Iwanowo-Wosniessensk* 6, 406; *Chem. Zentr.* 1922, III, 326; cf. preceding abstr.—It is shown that the diffusion of gas through porous substances follows the Bunsen law only in exceptional cases and is independent of the opposing diffusion of other gas. On the surfaces of inlet and outlet a "jump" of the gas pressure occurs which is always greater at the outlet surfaces than at the inlet surfaces and at the latter can even be negative. The relation between the strength of the gas current and the difference in pressure is not linear.

C. C. DAVIS

The molecular state of pure liquids. IV. The relation between surface tension, molecular weight and the number of atoms in the molecule. P. N. PAVLOV. *J. Russ. Phys. Chem. Soc.* 49, 304-7(1917).—P. deduces that the surface tension of normal liquids at corresponding states (corr.) is proportional to the product of the mass of the mols. times the square root of the no. of atoms in the mol., i. e., $\gamma_{corr.}/M\sqrt{n} = \text{const.}$ $M = \text{mol. wt.}$; $n = \text{no. of atoms in the mol.}$ Tables show that this law holds within 0.1-0.2% for the normal liquids Et_2O , CCl_4 , Pr formate and its homologs. The const. deviates for benzene, $AcOH$, and $MeOH$. The molecular state of liquids from the function $M\sqrt{n}/\gamma_{corr.} = \text{constant}$. *Ibid* 307-8.—In associated liquids γ is increased while in dissociated liquids γ is decreased. Hence for an associated liquid the function $M\sqrt{n}/\gamma$ must be smaller than that for a normal liquid and greater than normal for a dissociated liquid. V. The relation between density, absolute temperature and

number of atoms in the molecule. *Ibid* 309-11.— $d_{corr} \sqrt{n}/T_{corr} = \text{const.}$ (1) A table shows that this holds for CCl_4 , Et_2O , AcOEt , HCOOMe , and AcOPr . From the equation and the table the d of a liquid can be calcd. if the critical temp. is known. G. G. Longinescu (*Ann. sci. Univ. de Jassy* 1, 359(1901); 2, 126(1903)) by empirical reasoning developed a formula similar to (1) in which d signified the density of the liquid at 0° and T the abs. temp. of the boiling liquid at atm. pressure. Formula (1) is more logical since it compares liquids at corresponding states. VI. The dependence of the corresponding temperature upon the molecular weight and the number of atoms in the molecule. *Ibid* 311-5.— $\gamma/T_{corr} = K_1$. Combining this with $M\sqrt{n}/T_{corr} = K_2$, $M\sqrt{n}/T_{corr} = K$ (1). That is, the corresponding abs. temp. of normal liquids is proportional to the product of the mol. wt. and the square root of the no. of atoms in the mol. If equation (1) is rearranged thus: $T_{corr} = M\sqrt{n}/K$, it is seen that the T_{corr} of a normal liquid is higher the greater the mol. wt. and no. of atoms in the mol. This dependence of T_{corr} on the mol. state of the liquid leads to the deduction that the function $M\sqrt{n}/T_{corr}$ is less than its value for normal liquids when there is association and greater when there is dissociation. This equation is useful in detg. the state of liquid if the crit. temp. is known. The relations between critical temperature and the molecular weight and number of atoms in the molecule. *Ibid* 315-6.—From $M\sqrt{n}/T_c = K$, in which $T_c = \text{crit. temp.}$, it follows that $T_c \propto M\sqrt{n}$. For CCl_4 , $T_c = M\sqrt{n}/0.6185$ (3). That is, in a homologous series of normal liquids an increase of mol. wt. is accompanied by an increase of T_c . Hence if there is association or polymerization of a mol., *i. e.*, increase of M and n , a greater T_c results as compared with the value of T_c for normal liquids. If dissociation of the mol. occurs, T_c is lower as compared with normal liquids. Thus T_c calcd. for H_2O by formula (3) is 50.407° ; actually T_c for H_2O is 647° . Hence water is associated. T_c calcd. for $n\text{-C}_8\text{H}_{18}$ is 939.81 . Actually T_c is 569.2 . Hence octane is dissociated. This formula also enables one to estimate the mol. condition of metals assuming that their behavior is similar to that of a normal gas. The molecular state of liquids according to the function, $M\sqrt{n}/T_c$. *Ibid* 317.—A liquid is normal if $M\sqrt{n}/T_c = 0.6185$, associated if $M\sqrt{n}/T_c < 0.6185$, dissociated if $M\sqrt{n}/T_c > 0.6185$. Liquids are considered normal which do not differ more than 2% from the value for CCl_4 . Of 188 liquids examd. 8 are normal, 92 associated and 88 dissociated. VII. The molecular volume of normal liquids. *Ibid* 318-21.—It is developed mathematically that normal liquids at similar pressures and temps. have the same number of mols. in the same vol.

GEORGE W. PUCHER

The constitution and structure of flowing masses of water. GRAEVELL. *Wasser* 18, 62-4; *Chem. Zentr.* 1922, 111, 485.—Mols., aggregates, resistance to friction, transportation of suspended matter, etc., in flowing H_2O are explained mathematically and physically.

C. C. DAVIS

Dialysis of small volumes of liquids. The lily-pad dialyzer. R. W. WOOD. *J. Phys. Chem.* 27, 565-6(1923).—A few drops of collodion which has been thinned with ether are poured on a glass plate. The plate is rotated and by means of a small stick the collodion pool is shaped into a disk with a thickened edge. The disk is allowed to dry and is then removed with water. The liquid to be dialyzed is placed in the disk and the whole floated on water. A disk 4 cm. in diam. will hold up 2 cc. of soln.

R. F. SCHNEIDER

The colloidal nature of sulfur in ultramarine. I. F. KEME. *Chem.-Ztg.* 47, 513(1923).—From a general statement by Ostwald (*cf. Die Welt der vernachlässigten Dimensionen*) that alkalis increase the dispersion of both inorg. and org. highly dispersed S systems, it is suggested that S can be dispersed more highly by the action of an alkali. To this end ultramarine was fused with an alkali, whereupon the blue was transformed to a deep red. This expt. indicates that the S of ultramarine is in colloidal soln.

C. C. DAVIS

The swelling of agar-agar. F. FAIRBROTHER AND H. MASTIN. *J. Chem. Soc.* 123, 1412-24(1923).—Agar appears to consist principally of the Ca salt of an acid sulfuric ester, $(\text{ROSO}_2)_2\text{Ca}$. The effect of acid is to produce a reversible equil. of the type, $(\text{ROSO}_2)_2\text{Ca} + 2 \text{HCl} \rightleftharpoons 2 \text{ROSO}_2\text{H} + \text{CaCl}_2$, the Ca salt and the free acid ester being somewhat ionized. The free acid swells less in H_2O than the Ca salt and its ionization and swelling are further diminished by the presence of acid. The K salt forms a very firm gel. The free acid ester decomposes on heating. Agar differs from gelatin with respect to swelling in acid and alk. solns. Acids decrease the swelling, an effect nearly proportional to the p_H . The effects of HCl , H_2SO_4 , $\text{H}_3\text{C}_2\text{O}_4$, AcOH , and H_3PO_4 are almost the same at the same p_H . The swelling of agar in dil. NaOH ($N/800\text{-}N/25600$) solns. is greater than in H_2O , but in more concd. NaOH solns.

(*N*/6.25-*N*/400) and in Ba(OH)₂ solns. is less than in H₂O. The results support the view that swelling of agar is governed by a chem. reaction between the medium and the acid ester. The behavior of agar as an electroosmotic diaphragm further supports the theory that the framework of an agar gel consists of hydrated undissociated sulfuric esters and the electronegative sulfuric ester complex. H. B. LEWIS

The properties of some silver organosols. J. K. GILES AND C. S. SALMON. *J. Chem. Soc.* 123, 1597-1608(1923).—All methods of prep. Ag organosols give sols contg. other substances than Ag and the org. liquid. Some of these other substances are probably necessary for stability of the sol. An *app. for prep. pure Ag sols in org. liquids* by the arc process is described. Two Ag tubes are soldered together in the form of a vertical cross, one in front of the other, and communicating through a small hole. The horizontal tube contains the Ag arc, the vapors from which are blown by a stream of N₂ through the hole into the org. liquid contd. in the vertical tube. The liquid comes in contact only with Ag. *Ag sols in alc.*—No stable sols could be obtained in abs. alc., sols being considered stable if they gave no ppt. in two days. Addn. of 15% H₂O gave a stable sol. Addn. of substances such as acids, bases, and bromobenzene which stabilize the sol in H₂O do not give stable sols in abs. alc. The small amt. of rubber dissolved from stoppers by alc. readily stabilizes the sol. *Ag sols in stearic acid.*—Ag stearate was dissolved in stearic acid at 180° and reduced by passing H₂ through. Dark red sols contg. as high as 10% free Ag were obtained. Analysis showed that 84.9% of the Ag is reduced in 5 hrs. and 91.2% in 16 hrs., giving stable sols. After 24 hrs. passage of H₂ the Ag is completely reduced and has settled out completely. Small amts. of Ag stearate are sufficient to peptize large amts. of Ag, but a stable sol cannot be prepd. in the total absence of Ag stearate. At 80° cataphoresis expts. showed no motion of the particles. The sp. cond. of solns. of Ag stearate in stearic acid and of the Ag sols is of the order of 2.10⁻¹¹ reciprocal ohms. The surface tensions at 138° by the capillary tube method for stearic acid, 2% Ag stearate in stearic acid, and the Ag sols are 22.7, 22.6 and 21.0 resp. The viscosities stand in the proportion of 144.0, 147.7, and 144.4 resp. NaCl and HCl coagulate the sol. Na₂SO₄ does not. Stable sols result when the Ag sol in stearic acid is dissolved in paraffin wax, ligroin, hexane, toluene, benzene, and amyl acetate. The following cause pptn.: xylene, ethyl alc., amyl alc., and ether. Acetone pptd. part and gave a stable sol of the remainder. The sols in acetone and amyl acetate are negatively charged. Stable Ag sols were prepd. by the analogous methods in lauric, palmitic, and margaric acids. The sols in *n*-octoic, valeric, and acetic acids are stable for 25, 10 and 0 min. resp. Stable sols are formed only when a polar substance is present contg. radicals similar to those in each of the 2 phases. Stability is due to adsorption at the interface with surface orientation after the ideas of Langmuir and of Harkins.

F. L. BROWNE

The protective action of potassium oleate on gold sols in water-alcohol mixtures. E. K. RIDGAL AND L. L. BIRUMSHAW. *J. Chem. Soc.* 123, 1565-70(1923); cf. *Iredale, C. A.* 15, 2758.—The protective action of K oleate on Au sols prepd. in alc.-H₂O mixts. decreases with increasing alc. content, exhibiting 3 well defined ranges, 0-10%, 10-26%, and 26-45% by vol. Above 50% alc. the soln. exerts no protective action. By comparing the protective action with the alteration of the viscosity and the surface tension of such solns. as observed by Bircumshaw, *C. A.* 17, 1570, it is shown that the capillary active material, either the colloidal or micellar form, is the protective agent. The surface concn. of soap at the Au-liquid interface apparently runs parallel to the surface concn. at the liquid-air interface. The hypothesis is advanced that the colloidal form is more protective than the micellar and that the micellar form disappears at about 26%, the colloidal form remaining up to about 50%.

F. L. BROWNE

Colloidal clay. D. CASIMIRO BURGUES Y ESCUDER. *Mem. acad. cienc. artes* 17, No. 19, 18 pp.(1922).—Ten-g. portions of air-dried, 1 mm.-mesh clay were shaken with 200 cc. 1:1000 soln. of different dyes, and the amt. of unadsorbed dye remaining in each soln. was detd. colorimetrically. Following is the vol. of 1:1000 dye soln. which, if dild. to 50 cc., would match the color of the soln. of unadsorbed dye: "Crystal violet O," 4 cc.; "coned. acid green," 10 cc.; "dianiline red," 10 cc. "Methylene blue DBB" was almost completely adsorbed, and "fuchsin in large crystals" even more so. If 5-g. portions of clay were used, 7 cc. and 2 cc., resp., of methylene blue and fuchsin, when dild. to 50 cc., matched the colors of the unadsorbed dyes. The presence of CaCO₃ in the clay did not alter its power to adsorb methylene blue. Other expts., not detailed, indicate that the amt. of dye adsorbed by a clay is not a satisfactory quant. measure of the colloidal matter in the clay, because other components of the clay may also adsorb dye. This paper is largely a resumé of the work of others.

R. H. LOMBARD

The effects of electrolytes on gelatin sols. A. P. IVANITZKA. *Nachr. Phys.-Chem. Lomonossov Ges. Moskau* 1, No. 2, 104-36(1920); *Chem. Zentr.* 1922, III, 678-9.—An investigation of the Hoffmeister series shows that the effect of anions on surface tension and internal friction depends upon the concn. and does not always follow the Hoffmeister series. An increase in Γ const. does not require unconditionally a decrease in the other, contrary to the theory of Gibbs. The effect of anions on the velocity of gelatinization generally follows the Hoffmeister series and only at very high or very low concns. do deviations occur. C. C. DAVIS

The reciprocal displacement of a substance carried down by a precipitate. ANDRÉ CHARRIOU. *Compt. rend.* 176, 1890-1(1923); cf. *C. A.* 17, 1930.—Chlorides, bromides, iodides, nitrates, and acetates did not displace the yellow chromate carried down by pptd. alumina. Carbonates, sulfides, sulfates, oxalates, tartrates, citrates, phosphates, and arsenates entirely displaced the chromate. The results are generalized as follows: a substance carried down by a ppt. is displaced on that ppt. by a substance of the same kind but having a higher valence. A substance will not displace another of higher valence. If the 2 substances have the same valence, the less concd. is displaced by the more concd. H. M. McLAUGHLIN

Isotherms for the adsorption of salts by manganese dioxide. MAX GELOSO. *Compt. rend.* 176, 1884-7(1923).—The adsorption of Cu and Ni by MnO_2 was analogous to that of Fe (cf. *C. A.* 16, 3018). The exptl. results are expressed by $\gamma = KC^m$, where C is the concn. in mg. mols. per l. of the salt in soln. after adsorption is completed. $\gamma = n/(n+n')$, where n is the no. of mg. mols. adsorbed and n' is that of the adsorbent and $m < 1$. The curves showing the relation between $\log \gamma$ and $\log C$ for the 3 metals are parallel straight lines. For Fe, $\gamma = 0.057 C^{0.31}$; for Cu, $\gamma = 0.027 C^{0.32}$; and for Ni, $\gamma = 0.014 C^{0.31}$. H. M. McLAUGHLIN

New adsorption calculations. L. BERÉNYI. *Z. physik. Chem.* 105, 55-72(1923); cf. *C. A.* 16, 3241.—The recent adsorption measurements of Patrick and his co-workers and of Bert and Andress (*C. A.* 17, 1677) have been computed from the standpoint of the Polanyi (*C. A.* 16, 3784) theory of adsorption. H. JERMAN CREIGHTON

The origin of osmotic effects. IV. Hydronodynamic change in aqueous solutions. H. E. ARMSTRONG. *Proc. Roy. Soc. (London)* 103A, 610-8(1923); *Compt. rend.* 176, 1892-4(1923).—A simple explanation may be given for the process of dissolving salts in water which accounts equally well for elec. and osmotic peculiarities. "Water" is a complex satd. with the "gas" hydrone, OH_2 . The vapor pressure either of water or of a soln. is the measure of the proportion of free hydrone mols. present. If the proportion of free hydrone mols. were large in ordinary water, the b. p. should be much lower. Any solute lowers the vapor pressure and establishes a negative pressure in the liquid. Each mol. of solute appears to "anchor" a mol. of hydrone. Nonelectro-

lytes all have unit effect per mol. proportion. They form a simple hydrol, $M \begin{matrix} H \\ \diagdown \\ \diagup \\ OH \end{matrix}$.

With electrolytes, not only is the solute hydrolated but it is itself distributed upon hydrone. The salt RX forms the reciprocal systems, $RX \begin{matrix} H \\ \diagdown \\ \diagup \\ OH \end{matrix}$ and $H_2O \begin{matrix} R \\ \diagdown \\ \diagup \\ X \end{matrix}$. With

diln. the former is changed more and more to hydronol, $H_2O \begin{matrix} H \\ \diagdown \\ \diagup \\ OH \end{matrix}$. Finally, the soln.

contains solute only as $H_2O \begin{matrix} R \\ \diagdown \\ \diagup \\ X \end{matrix}$ with an equal no. of mols of hydronol. The "distributed" reciprocal complexes, including hydronol, are the electro-chem. agents. The negative radical in such complexes has greater residual affinity than it has in the original mols. When a soln. is in contact with water, each of the complexes, $HCl \begin{matrix} H \\ \diagdown \\ \diagup \\ OH \end{matrix}$,

$H_2O \begin{matrix} H \\ \diagdown \\ \diagup \\ Cl \end{matrix}$, etc., attracts a mol. of hydrone and thus reestablishes the equilibrium of hydrone in the soln. Osmotic pressure is the hydraulic pressure exercised by the extra mols. of hydrone attracted into the soln. by the distributed complexes. H. M. McLAUGHLIN

Atomic volume and solubility. R. FLATT. *Helvetica Chim. Acta* 6, 698-707 (1923).—F. makes use of Bodlander's equation for calcg. the soly. of inorg. salts in water

and also for calcg. the energy of formation of salts. F. develops the formula $\bar{P} = (Q_b + Q_a) - Q_{ba}$ in which P is the difference of the energy Q_{ba} and the heats of hydration of the gaseous ions Q_b and Q_a . If P is large the soly. is large and if P is small the soly. is small. This equation has been applied to alk. earth sulfates, perchlorates, etc., and agrees very closely with the exptl. values.

R. F. SCHNEIDER

The influence of a third substance upon the miscibility of phenol and water. A. BOUTARIC AND (MILLE.) Y. NABOT. *Compt. rend.* 176, 1618-20 (1923).—The presence in phenol (or water) of a third substance which is insol. in water (or phenol) diminishes the soly. of water in phenol or *vice versa*. The temp. of the mixt. is increased in proportion to the amt. of the third substance added. Salol, azobenzene, anthraquinone, naphthylamine, and naphthalene were the substances added to the phenol-water mixts.

R. F. SCHNEIDER

Piezo-chemical studies. XIX. Experimental determination of the fictive volume change in solution equilibrium. ERNST COHEN AND A. L. TH. MOESVELD. *Z. physik. Chem.* 105, 145-54 (1923); cf. *C. A.* 17, 2528.—A mathematical and theoretical paper in which 4 methods for the exptl. detn. of the fictive vol. change in solu. equil. are described. Two of these methods (a volumetric and an elec. method) have been discussed previously; the other two (also a volumetric and an elec. method) are new. **XX. Experimental proof of Braun's law by an electrical method.** II. ERNST COHEN, F. ISHIKAWA AND A. L. TH. MOESVELD. *Ibid* 155-72.—Exptl. quant. examn. of Braun's law for electrolytes has shown that this relation describes the facts within the limits of exptl. error. In order to carry out this examn. the authors have detd.: (1) the temp. coeff. of the soly. of Th_2SO_4 ; (2) the pressure coeff. of the soly.; (3) the fictive vol. change (elec. method); (4) the fictive heat of soln. (elec. method).

H. JERMAIN CREIGHTON

The theory of acid-alkali solution equilibrium as applied to salts of moderately strong but sparingly soluble acids. E. B. R. PRIDEAUX. *J. Chem. Soc.* 123, 1624-34 (1923).—Equations have been deduced for calcg. the H ion concn. which occurs at the end point in the neutralization of a mixt. of a strong acid with a fairly strong but sparingly sol. acid having a dissociation const. not exceeding 10^{-4} . The predicted results have been tested exptl. in the case of benzoates and salicylates and partly confirmed. Rapid methods have been described for the titration of both total alkali and acid in benzoates and salicylates.

F. L. BROWNE

Studies in the kinetics of reactions. I. H. V. EULER AND ERIC G. RUDBERG. *Z. Physik* 16, 54-62 (1923).—The writers discuss the reversible reaction between AcOH and H_2O in the presence of HCl as a catalyst, under the assumption that the active agents in the reactions are the positive ions of the oxonium salts of the ester and of alc. or AcOH . From the reaction velocity and the estd. concn. of these ions, it seems likely that the velocity const. for the dissociation of ionogens (e. g. the mols. of a salt) is of the order of 10^8 —too high to measure. In the conversion of α - into β -glucose in the presence of alkali, the active mols. are very likely negative ions corresponding to the formation of an (oxonium?) acid from glucose, with ionization const. $K_a = 6.6 \times 10^{-13}$. If so, data show that K_w/K_a is independent of temp.; it follows that the degree of hydrolysis of Na glucosate is independent of temp., the heat of hydrolysis is zero, etc. Also, the reaction velocity as the temp. is changed should be proportional to K_w ; this is shown to be supported by the exptl. data. Similar relations hold for the acid hydrolysis of ethyl acetate, K_a for this compd. rising with the temp. at about the same rate as K_w . The degree of hydrolysis should in this case increase somewhat with temp., however, as the heat of hydrolysis is positive. Cf. *C. A.* 14, 3410; 17, 2530.

R. S. MULLIKEN

Catalysis. XV. Some induced reactions and their analogy in the animal body. N. N. MITTRA AND N. R. DHAR. *Z. anorg. allgem. Chem.* 122, 146-50 (1922).—A further study of induced reactions (cf. *C. A.* 12, 111; 15, 3237), including those in which oxidation is accelerated or retarded by secondary compds. The following inorg. reactions were studied, the first pair of compds. comprising the primary reaction, the others the secondary (O means atm. O): HgCl_2 (I) + Na_2SO_4 (II), I + Na_2AsO_4 (III); I + HCO_2H , I + III; I + Na_2HPO_4 , I + III; I + II, I + H_2AsO_4 ; I + Na_2HPO_4 , I + H_2AsO_4 ; II + O, NaNO_2 + O; II + O, $(-\text{CO}_2\text{K})_2$ (IV) + O; II + O, $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$ + O; II + O, $\text{Co}(\text{OH})_2$ + O; II + O, $\text{Ni}(\text{OH})_2$ + O; H_2SO_4 + O, FeSO_4 + O; $\text{Fe}(\text{OH})_2$ (V) + O, IV + O; H_2SO_4 + O, SnCl_2 + O; V + O, $\text{Ni}(\text{OH})_2$ + O; $\text{Co}(\text{OH})_2$ + O, $\text{Ni}(\text{OH})_2$ + O; $\text{Mn}(\text{OH})_2$ + O, $\text{Ni}(\text{OH})_2$ + O; $\text{Ce}(\text{OH})_2$ + O, $\text{Ni}(\text{OH})_2$ + O; II + O, III + O; II + O, $\text{Mn}(\text{OH})_2$ + O; II + O, $\text{Na}_2\text{S}_2\text{O}_4$ + O; SnCl_2 + O, $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$ + O. The primary reactions in the first 17 were accelerated, in the last 4 were retarded by the second compd. Oxidation of the following compds. by atm. O was induced either by

the oxidation of V (freshly pptd. and free of alkalis) in aq. suspension or in the presence of II (which was itself oxidized) with CO_2 as the end product: $\text{CO}(\text{NH}_2)_2$, starch, grape sugar, cane sugar, IV, NaOAc , K Na tartrate, HCO_2Na , Na citrate, Me_2CO , chloral hydrate, glycerol, quinine sulfate, $(-\text{CH}_2\text{CO}_2\text{Na})_n$, MeOH, EtOH, PhOH, phenolphthalein and gum arabic; the following by II but not by V: CHCl_3 , glutaric acid, maltose, K stearate, cholesterol, anthraquinone, PhNHCOMe and brucine; PhCO_2Na by V but not by II. MeOH, EtOH, AmOH, glycerol, glutaric acid, PhOH and brucine were induced by II or V and gave both CO_2 and an aldehyde as products. BzOH on oxidation gave an acid reaction to litmus. Since proteins, carbohydrates, fats, etc., cannot be readily oxidized directly by O but are easily oxidized to CO_2 in the animal body, it is suggested that *oxidation in the body* is accelerated by some form of induced reactions analogous to those described, perhaps by formation of peroxides which in turn oxidize directly the nutrient. Since it has been shown previously that oxidation by peroxides is accelerated by Fe salts, it is further suggested that Fe in the blood plays the role of a catalyst, and that a deficiency (anemia) means that no induced reaction can take place. *The role of Fe compds. in medicine* is probably that of inducing such reactions.

C. C. DAVIS

Catalysis. XX. The relation between the order of a reaction and its temperature coefficient. N. R. DHAR. *Z. anorg. allgem. Chem.* 128, 218-28(1923).—An examn. of the literature on temp. coeffs. of reactions and the order of the reactions shows that the temp. coeff. is higher the lower the order of the reaction. In making this comparison the true order of the reaction must be considered, not the apparent order. **XXI. Neutral salt action.** *Ibid.* 229-40.—Studies were made of the influence of neutral salts on the velocities of the reaction between (a) oxalic acid and chromic acid, (b) formic acid and chromic acid, (c) Na formate and I_2 , (d) Na formate and HgCl_2 , (e) Na formate and AgNO_3 . The action of the neutral salt is more pronounced in dil. soln. The action of different salts is highly specific. With all the reactions some salts retard and others accelerate the reaction. The presence of the neutral salts does not alter either the order of the reactions or their temp. coeff. Similar effects of neutral salts on physiol., chem. and phys. processes have been observed by numerous authors, a list of 21 such processes being given.

F. L. BROWNE

The kinetics of dehydrogenization catalysis. N. ZELINSKŪ AND N. PAVLOV. *Ber.* 56B, 1249-55(1923).—The degree of dehydrogenization of cyclohexane by finely divided Pt, Pd, and Ni at 150-400° was measured. The results are given in 6 tables and 2 graphs. The vol. of H_2 liberated and the refractive index of the resulting mixts. were measured to det. the degree of dehydrogenization. Pt and Pd were found to be very efficient, while Ni, because of side reactions and the coating of C deposited on it, was only about 20% as active as Pt or Pd.

E. N. BUNTING

Equilibrium between reducing gases and metallic oxides. I. (1) Carbon monoxide and tin oxide. (2) Carbon monoxide and zinc oxide. TSUYOMU MAEDA. *Bull. Inst. Phys. Chem. Res. (Japan)* 2, 350-61(1923).—The equil. which can be obtained in the reduction of SnO_2 and ZnO with CO has been studied. The CO is passed over SnO_2 , contained in an alundum combustion boat and heated at 700-950° in a porcelain tube, with a velocity less than 1 cc. per min. Within the above temp. range SnO is unstable and decomposes as follows: $2\text{SnO} \rightarrow \text{SnO}_2 + \text{Sn}$. At the same temps., the equil., $\text{SnO}_2 + 2\text{CO} = \text{Sn} + 2\text{CO}_2$, is established and defined by the following expression: $\log K = -0.41.8/T + 1.084$. The reaction heat at 800° is -5870 cal. For Sn(liquid) + $\text{O}_2 = \text{SnO}_2$ at 800° $\Delta H = -130,260$ cal. The pressure of O_2 evolved from SnO_2 at 927° is 4.47×10^{-14} . By the same process, CO was passed over ZnO , but the reaction was not definitely examd., inasmuch as the reducing efficiency of CO is much less than that in the case of SnO_2 . The vol. percentages in the resultant gases were 4.5, 6.0, and 6.5 at 741°, 827° and 859°, resp. The O_2 pressure of ZnO at 827° was about 1.6×10^{-20} .

K. KASHIMA

The system copper oxide, copper hydroxide, cuprite, sodium hydroxide. ERICH MOLLER, et al. *Z. physik. Chem.* 105, 73-118(1923).—Blue $\text{Cu}(\text{OH})_2$ dissolves in concd. NaOH soln. in considerable quantities to form deep blue solns., from which a black-brown ppt. gradually separates, provided the concn. of the NaOH does not exceed 17N. Any $\text{Cu}(\text{OH})_2$ remaining undissolved gradually turns brown. This dark colored substance is regarded as a solid soln. of CuO and $\text{Cu}(\text{OH})_2$, the content of the latter depending on the Cu concn. of the soln. in which it is contained. Dehydration of the $\text{Cu}(\text{OH})_2$ contained in these solid solns. takes place gradually, but the resulting product is not water-free CuO . The soly. of both CuO and $\text{Cu}(\text{OH})_2$ increases at first with the concn. of the NaOH and then falls off when a definite NaOH concn. is reached. The soly. of $\text{Cu}(\text{OH})_2$ is considerably greater than that of CuO . The max. solubilities

correspond to the transition points: $\text{CuO} \rightleftharpoons \text{cuprite}$ and $\text{Cu(OH)}_2 \rightleftharpoons \text{cuprite}$. A cuprite has been crystallized from alk. soln. It has a cobalt blue color and probably the compn. Na_2CuO_2 .

H. JERMAIN CREIGHTON

Some solidification curves of binary systems. MICHELE GIUA. *J. Am. Chem. Soc.* 45, 1725-7(1923).—Exception is taken to a statement by Bell (cf. *C. A.* 14, 347) and by Taylor and Rinckenbach (cf. *C. A.* 17, 870, 880) that G. in earlier researches (cf. *C. A.* 8, 2731; 9, 2089) assumes the temp. of solidification of binary mixts. to be the min. obtained by undercooling. Reply. JAMES M. BELL. *Ibid.* 1727. C. C. D.

The distillation of toluene with steam. J. BARBAUDY. *Compt. rend.* 176, 1616-8 (1923).—Toluene and water form a eutectic mixt. which boils at 84.34° (760 mm.) and contains 55.73 mol. % toluene. These results agree with those calcd. by means of Dupre's equation.

R. F. SCHNEIDER

The freezing-point curve for mixtures of potassium nitrate and sodium nitrate. H. V. A. BRISCOE AND W. M. MADGIN. *J. Chem. Soc.* 123, 1608-18(1923).—The f.-p. curve for mixts. of NaNO_3 and KNO_3 was detd., the cooling curve method being used, and found to be continuous with a min. at 225.7° and approx. 55% KNO_3 instead of meeting at a eutectic point as has been hitherto supposed. The cooling curves exhibit a sharp arrest at the initial f. p. but do not show a second arrest as would be the case if there were a eutectic point. An app. is described for separating the solid phase from the liquid mixt. with which it is in equil. Analysis of the solids in equil. with liquid mixts. near the compn. of min. f. p. shows them to be solid solns. differing little in compn. from that of the liquid. NaNO_3 and KNO_3 above 130° therefore form a continuous series of solid solns. and not a eutectic mixt. The m. p. of NaNO_3 is 309° \pm 0.5° and that of KNO_3 333° \pm 0.5°.

F. L. BROWNE

Physical and chemical transformations of the systems of Gibbs. TH. DE DONDRER. *Bull. acad. roy. Belg.* 1920, 315-28; *Chem. Zentr.*, 1922, III, 206.—A summary of the basic principles and the methods used in deriving phys. and chem. laws of the heterogeneous systems investigated by Gibbs. Contrary to other authors who have investigated systems in equil., transformations are used as a basis for investigation. C. C. D.

Cryoscopic investigations of some solutions in bromine. WALDIMIR FINKELSTEIN. *Z. physik. Chem.* 105, 10-26(1923).—The empirical value of the cryoscopic const. for Br is $K = 83.07$; the theor. value, $K = 86.35$. According to cryoscopic measurements, the nonelectrolytes AsBr_3 , CCl_4 and S_2Br_2 have in Br soln. mol. wts. which are identical with their formula wts.; while in the same solvent the mol. wts. of AlBr_3 and $\text{CBr}_4\text{CO}_2\text{H}$ are double the formula wts., the polymerization coeff. being const. for all concns. Owing to polymerization and solvation, the conducting substances PBr_5 , CH_3CONH_2 and SbBr_3 form complexes in Br soln., the compn. of which varies with the concn. of the soln. The cond. of the solns. studied is closely associated with the formation of complicated complex mol.

H. JERMAIN CREIGHTON

A relation between the absolute melting point, boiling point and critical temperature of substances. EDM. VON AUBEL. *Bull. acad. roy. Belg.* 7, 460-72; *Chem. Zentr.* 1922, III, 227.—The value of the const. r in the equation of Prud'homme (cf. *C. A.* 15, 784) is calcd. for numerous substances and found to be approx. 1 for HgCl_2 , HgBr_2 , HgI_2 , SbCl_3 , AlBr_3 and AlI_3 . For metallic Hg, on the other hand, it was only 0.512.

C. C. DAVIS

A simple relation between the specific heats of liquids, especially condensed gases. VICTOR FISCHER. *Z. ges. Kalte-Ind.* 29, 128-9(1922); *Physik. Ber.* 3, 1091-2(1922).—By a no. of examples it is demonstrated that for 1-, 2- or 3-at. liquids, the sp. heat at the normal b.p. can be represented with good approximation by the formula $6n/m$, where n is the mol. no. and m the mol. wt. of the liquid. Nothing is said of the temp. influence on sp. heat.

A. E. STERN

The specific heats of solutions of calcium and magnesium chlorides at medium and low temperatures. WERNER KOCH. *Z. ges. Kalte-Ind.* 29, 37-43; *Chem. Zentr.* 1922, III, 905.—The sp. heats were detd. by the Pfundler method, with an elec. unit immersed in the soln. The results are given in tables and curves.

C. C. DAVIS

The valence energy of hydrocarbons. J. P. WIBAUT. *Chimie et industrie, Special No.*, 178-85(May, 1923); cf. *C. A.* 17, 1915.—A study of the heat of combustion of hydrocarbons shows that there is a relation between the energy of a simple C linking and that of a double linking. The difference between two simple linkings and a double linking is about 18 cal. in the olefin series, about 12 cal. in the cyclohexane series, and about 7 cal. with aromatic hydrocarbons. The min. heat of formation of a simple linking can be estd. at 70 cal. from Fajan's work on the heat of sublimation of diamond (*C. A.* 14, 1623-4, 3086-8). It follows that the energy of a double linking is about 120 cal., and of a triple linking about 180 cal. Hence, the combination of two CH_2

groups to C_2H_4 gives off much more heat than the combination of two CH_2 groups. This depends entirely on the min. heat of formation of a simple linking. Thermochemically nothing indicates that there is a tension in polymethylene rings from cyclobutane to cycloheptane. These conclusions are in disagreement with Baeyer's tension theories.

Chemical constants of diatomic molecules. R. R. S. COX. *Proc. Cambridge Phil. Soc.* 21, 541-51(1923).—C. calcs. Γ , the chem. const. for diatomic gases, according to the statistical formula derived by Ehrenfest and Trkal, and Fowler. These values are compared with those obtained from values of the disson. const. K_p and also from vapor pressure measurements. The calcs. are made for I_2 , Br_2 , Cl_2 and N_2 , in the latter case on the basis of vapor pressure only. Except in the case of N when Γ (vapor pressure) is -0.15 and Γ (theoretical) is -0.16 , the agreement is very poor. The discordance may perhaps be explained on a theoretical basis, or it may be due to a lack of accurate knowledge of the values of p , K_p , and the sp. heats of the vapor and solid at low temps. This cannot be detd. until further measurements of these quantities have been made.

Electrolysis of ammonium chloride solutions. HASHMAT RAI. *Proc. 7th Indian Sci. Cong.* 1921, lxxviii-ix.—The anode potentials were measured under varying conditions to det. whether they agreed with those calcd. by Haber and Russ by the equation $e = K_1 \log I - K_2$ (where e = anode potential and I = current). Two procedures were used: I. A porous earthenware diaphragm and Pt foil anode with varying current strength. Light had a disturbing influence on the measurements. At the end of the expt. the liquid at the anode had a yellowish color, biting taste and pungent odor, was acid to litmus, indigo and Congo red and liberated I from KI. It probably contd. NCl_3 . The cathode liquid was colorless and had an odor of NH_3 . The anode gas was nearly all N and contd. less than 0.2% O. The cathode was mostly H. High current d., low temp., high concn. and absence of light were the chief factors favoring the formation of NCl_3 . The anode potential and the oxidizing power of the anode liquid increased uniformly with time and current d. The values of the anode-e. m. f. with varying current strengths agreed with those calcd. by Haber and Russ. II. Electrolysis in the dark in acid soln. with Pt gauze anode and without a diaphragm. The anode-e. m. f. detns. were made with varying current strengths and concns. The anode e. m. f. increased with time and current strength, but decreased with increase in concn. The formula of Haber and Russ was valid for these conditions also.

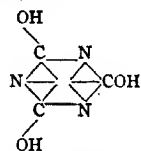
Active hydrogen by electrolysis. V. VENKATARAMAIAH AND BH. S. V. RAGHARA RAO. *Nature* 112, 57(1923).—Contrary to Wendt and Landauer and to former expts. by V., it is found that H is actually activated when a conducting soln. is electrolyzed. The failure of expts. with a metal and acid seems to be due to decomn. of active H by the spray with the formation of H_2O_2 . Cf. Grubb, *C. A.* 17, 2804. G. L. CLARK

Application of Bjerrum's theory of electrolysis to the diffusion of electrolytes and the potential of diffusion. ERLING SCHREINER. *Tidsskrift for Kemi og Bergvaesen* 2, 151-3(1922).—As it appears that the osmotic const. can be approx. expressed as a linear function of the concn. $K_0 = \alpha + \beta\sqrt{C}$, S. has set up a new formula for the osmotic coeff.: $f_2 = 1 + \alpha C^{\frac{1}{2}} + \beta C^{\frac{3}{2}}$ and corresponding formulas for the diffusion coeff. and the diffusion potential. CHR. H. A. SYVERTSEN

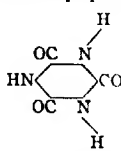
The hydrogenation potential of alloxanthine. EINAR BILMANN AND HAKON LUND. *Ann. chim.* 19, 137-44(1923).—Bilmann (*C. A.* 15, 2074) detd. the hydrogenation potential of quinhydrone and showed that the latter may replace the usual H electrode. Alloxanthine is chemically similar and should display the same properties. A quantity of solid alloxanthine was carefully purified by washing in a special type of electrolytic cell, contg. 2 Pt electrodes, and the potential π of the couple Pt | solid alloxanthine, 0.1 N H_2SO_4 | 0.1 N H_2SO_4 , H_2 | Pt was measured. At 18°, π was 0.3696 v; at 25°, π was 0.3664 v. With 0.02 N H_2SO_4 , π at 18° was 0.3700, indicating that π was independent of p_H . The H pressure equiv. to this potential was calcd. to be, at 18°, $10^{-12.8}$ atm., and at 25°, $10^{-12.4}$ atm. A comparison of the hydrogenation potentials indicated that the affinity of H for quinhydrone was much greater than that for alloxanthine. The hydrogenation potential of tetramethylalloxanthine at 18° was 0.3657 v. The substitution of Me for H has much more influence upon the hydrogenation potential in the alloxanthine than in the quinhydrone series, probably because hydrogenation in the former case is attended by a change in the nucleus. T. S. CARSWELL

Magnetic properties of cyanic and cyanuric derivatives. PAUL PASCAL. *Compt. rend.* 176, 1887-9(1923).—Since the groups CNO and $C_3N_3O_3$, play a const. magnetic

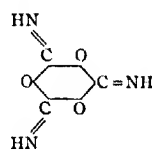
role, the application of the additive law permitted the calcn. of the part contributed by these groups in the mol. susceptibility of the corresponding acids, salts and esters. Metallic cyanates were shown to be isocyanates of the same type as the esters whose constitution ($O=C=N-R$) has been detd. by their chem. properties. Cyanuric acid, its salts and esters appeared to be substituted triazines with a nucleus having the same structure as C_3H_3 . The magnetic properties of $(C_3H_3O_3)$ in isocyanurates and cyamelide indicated the existence of identical bonds but corresponded to a satn. less than for cyanuric acid. These formulas are proposed:



Cyanuric Acid



Isocyanuric Acid



Cyamelide

H. M. McLAUGHLIN

Investigations on rotation dispersion. J. LIFSCHITZ. *Z. physik. Chem.* **105**, 27-54 (1923).—A theor. paper. The presence of a system of at least 4 coupled electrons, possessing only axial symmetry (an asym. electron system), is assumed to be a preliminary condition for the manifestation of optical activity. This system can be carried by either one or several atoms of the mol. In the first case the atom carrying the electron system is designated as the "asymmetric" atom. A narrow relation exists between absorption and the Cotton-effect. This effect is to be expected in those bands which go back to electrons of the "asymmetrical" (better axial-symmetrical) systems. An active mol. can contain several such systems; the rotation dispersion can, then, in consequence of "internal superposition," possess anomalous character. A series of heavy metal complex compds. and pure org. compds., all strongly absorbing substances, has been studied with reference to their rotation dispersion. The results obtained are discussed in connection with spectroscopic, photochem. and stereochem. knowledge.

H. JERMAIN CREIGHTON

Adiabatic transformations in the quantum theory and their treatment by Niels Bohr. P. EHRENFEST. *Naturwissenschaften* **11**, 543-50(1923).—Mathematical with an extensive bibliography. C. C. DAVIS

The quantum theory of polyatomic molecules. M. BORN AND E. HÜCKEL. *Physik. Z.* **24**, 1-12(1922).—The quantum theory of disturbed systems is applied to the calcn. of the rotational and vibrational motions in mols. containing more than one atom.

SAUL DUSHMAN

The quantization of rotating molecules. H. A. KRAMERS. *Z. Physik* **13**, 343-50 (1923).—The mol. is considered as a solid body inside of which an axially sym. circle is free to rotate about an axis held rigid in the mol. The equations of motion in such a system are developed according to classical dynamics and the quantum conditions are introduced that the total impulse moment must be an integral value of $h/2\pi$.

SAUL DUSHMAN

The thermoquantum. V. I. SHVONEN. *Ann. Acad. Sci. Fennicae* **15A**, No. 2, 43; *Chem. Zentr.* **1922**, III, 322.—Formulas are derived for thermochemically free energy, for the inner energy of compds. (termed by S. valence heat) and for chem. heat tone. To this end a quantum hypothesis is formulated according to which the rhythmic oscillations of the valence electrons stand in a simple energy relation to a H electron oscillating between its first and third quantum orbits. The basis of these periodic impulses of energy (termed by S. valence quanta) is the thermoquantum, which is 3.379 cal. per g.-mol. It represents a general thermochem. unit of energy. The valence of the various atoms is explained in its relation to the H quantum. C. C. DAVIS

High-speed cinematography and its application to the investigation of explosion phenomena and other very rapid reactions (CRANZ, BAMES) **24**. Filtration practice (WYNSIE) **13**. Analysis of bubbles in glass (RYDB, HUDDART) **19A**. Theories of magnetism (QUIMBY) (WILLS) (TERRY) **3**.

3—SUBATOMIC PHENOMENA AND RADIOCHEMISTRY

S. C. LIND

- Trends in photochemical research. J. H. MATHEWS. *Ind. Eng. Chem.* **15**, 885-7 (1923). E. J. C.
- The ether and electrons. OLIVER LODGE. *Nature* **112**, Suppl. No. 2805, 185-92 (1923).—An address. E. H.
- The relations of the atomic theory of Bohr to the explanation of chemical reactions. W. KOSSEL. *Naturwissenschaften* **11**, 598-604(1923).—A discussion and review. C. C. DAVIS
- The Bohr theory and radioactivity. G. VON HEVESY. *Naturwissenschaften* **11**, 604-5(1923).—A discussion. C. C. DAVIS
- Fluorescence of gases. J. FRANCK AND P. PRINGSHEIM. *Naturwissenschaften* **11**, 559-63(1923).—The application of the Bohr theory in explaining the fluorescence of gases. C. C. DAVIS
- The atomic theory of Bohr. MAX PLANCK. *Naturwissenschaften* **11**, 535-7 (1923).—A review with a portrait. C. C. DAVIS
- The quantum theory and the calculation of perturbations. MAX BORN. *Naturwissenschaften* **11**, 537-42(1923).—The analogy between at. and astronomic calcns. is discussed mathematically and diagrammatically. C. C. DAVIS
- Absorption and dispersion in the atomic theory of Bohr. R. LADENBURG AND F. REICHEL. *Naturwissenschaften* **11**, 584-98(1923).—Mathematical with an extensive bibliography. C. C. DAVIS
- The theory of Bohr and the collision of electrons. G. HERTZ. *Naturwissenschaften* **11**, 564-7(1923).—A review. C. C. DAVIS
- The principle of correspondence and the structure of the atomic shell. H. A. KRAMERS. *Naturwissenschaften* **11**, 550-9(1923).—A discussion with numerous diagrams. C. C. DAVIS
- Band spectra and molecular models. A. KRATZER. *Naturwissenschaften* **11**, 577-84(1923).—A mathematical review. C. C. DAVIS
- Röntgen spectra and the atomic theory of Bohr. D. COSTER. *Naturwissenschaften* **11**, 567-77(1923).—A review with diagrams and a bibliography. C. C. DAVIS
- Radiation and chemical reaction. H. S. HARNED. *J. Franklin Inst.* **196**, 181-202 (1923).—A comprehensive summary, with bibliography, of the hypothesis that radiation, by virtue of its power to bring molts. or atoms into an active state, is the cause of chem. reactivity. JOSEPH S. HEFBURN
- New conceptions in modern chemistry. G. URBAIN. *Technique moderne* **15**, 385-92(1923).—A review of the constitution and structure of atoms, and their relation to the properties of the elements. A. PAPINEAU-COUTURE
- The structure of the atom. N. BOHR. *Nature* **112**, Suppl. No. 2801, 29-44(1923); cf. *C. A.* **16**, 377, 2252.—English translation of Nobel prize address in which the important results obtained in recent years in the field of at. theory are summarized. G. L. CLARK
- Superconductors and the atom model of Rutherford-Bohr. H. KAMERLINGH ONNES. *Onnes Comm. Leiden*, Suppl. No. **44** to Nos. 157-63, 30-51(1921); *Physik. Ber.* **3**, 714-5(1923).—A discussion of previous exptl. and theoretical investigations, with some new data and points of view. The 3 super-conductors are Hg, Th and Pb, elements with at. nos. 80, 81 and 82. Ra G behaves like Pb. The discontinuity in transition to super-conductors is purely elec., just as that of the Curie point is purely magnetic. Regarding the relation to the Rutherford-Bohr atom the author limits himself to a series of unanswered questions. A. E. STERN
- Structure of the halides and oxides of the fifth, sixth and seventh groups. E. B. R. PRIDEAUX. *Chemistry & Industry* **42**, 672-5(1923).—A discussion. Structures for many compds. are suggested on the hypothesis of the single shared electron. This electrovalent bond abolishes a good many incongruities and awkward formulas in the groups mentioned but leads to difficulties in the lower groups. A. E. STERN
- Formula of carbon monoxide. G. W. F. HOLROYD. *Chemistry & Industry* **42**, 681-2(1923).—Thermochemical data support the formula :C:O: representing both atoms as surrounded by an octet. This is in agreement with the fact that in spite of the great affinity of C for O, CO is stable in air at ordinary temps., whereas NO is spontaneously oxidized although N has not much affinity for O. It is not possible to rep-

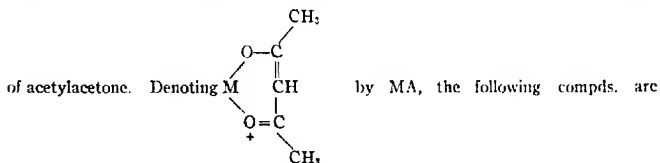
resent NO with a complete octet around each atom if only the electrons in the outer shell are employed.

A. E. STERN

Octet stability in relation to orientation and reactivity in carbon compounds. ROBERT ROBINSON. *Trans. Faraday Soc.* (advance proof) 1923.—R. seeks to dispel misunderstanding of Kermack and Robinson's explanation (cf. *C. A.* 16, 2633) of the alternating polarity effect on the basis of the octet theory. The word octet was not intended to have any precise implication as to no. or arrangement of electrons, but merely to denote a stable group. The explanation given assumed merely that the atoms in a C chain having the most nearly perfect octets act as if relatively electronegative, and are the most resistant to change. A C octet next to a strongly negative atom, like O, is thereby rendered imperfect, and weakened in its resistance to the tendency of the next C atom—and other outside atoms—to form a perfect octet.

R. S. MULLIKEN

The nature of the non-polar link. N. V. SIDGWICK. *Trans. Faraday Soc.* (advance proof) 1923.—S. discusses some applications to chem. facts of the theory that the non-polar valence bond is due to two "shared" electrons, the orbit of each of which includes the nuclei of both atoms—the recent Bohr atom being assumed. When one of the electrons is on the far side of one nucleus, the other electron is more nearly between the nuclei, and holds them together. At the same time, free rotation of the atoms is possible, in agreement with the facts in regard to single-bonded C atoms. The theory gives a phys. basis for the Baeyer strain theory. A C atom united to two others has two binuclear orbits connecting it to each; these are normally inclined at the angle of $109^{\circ}28'$. If these 3 atoms are joined in a ring of less than 5 atoms, the original angles must be changed, but the orbits will resist this change near the nuclei, and so will become curved. The double bond is an extreme case of the same type. The high distortion of the orbits here leads to high instability. The presence of two electron pairs between the nuclei also accounts for the observed restraint of free rotation of the atoms. Lowry's theory (*C. A.* 17, 2262) of the double bond (L. assumes one electron transferred, then a sharing of electrons) is inapplicable to C compds., whose polarity is in most cases not of the salt-like type but is a relatively small and probably secondary effect. Werner's coordination no. is really the no. of non-polar links that an atom is able to form (cf. Sidgwick, *C. A.* 17, 2668). The *effective at. no.* of an element in a compd. is defined as the total no. of electron orbits passing around its nucleus. The best evidence of high coordination nos. is provided by org. compds. of the "chelate" type, especially those



known: BeA_2 , $(BA_2)_2X$, AlA_3 , $(SiA_2)_2X$, $(TiA_2)_2X$, ZrA_4 , CeA_4 , ThA_4 . Since the metal M in MA is attached by two covalence bonds, the metallic atoms in the above compds. have respectively the covalencies or coordination nos. 4, 4, 6, 6, 8, 8, 8, 8. The covalence 6 does not appear (no BA_2 exists) until the second short period is reached; 8 does not appear before the second long period. In addition to examples above, OsF_8 and probably OsO_4 are octacovalent. A covalence of 10 may exist in some cases. It is concluded that the coordination no. is directly related to the size of the largest underlying completed quantum group, and cannot exceed by more than 2 the no. of electrons in each sub-group of such completed group. Dr. Plant's sodium pseudoindoxyl spirocyclopentane is formulated as a 4-covalent Na compd. of the chelate type. Other examples of this type are cited; all are β -atom rings contg. C, N or O (or both), and a metal atom.

R. S. MULLIKEN

The quantum theory of the complex Zeeman effect. A. M. MOSHARRAFA. *Phil. Mag.* 46, 177-93 (1923).—In a previous paper (*C. A.* 17, 2227) the theory of the Zeeman effect for H was developed from the standpoint of the quantum theory. To extend it to other elements the at. fields must be known. An exact theory of the at. and mol. structures of elements is the goal of spectroscopic research. So far the exact theory has been presented only in the case of the simple H atom. The general theory of Sommerfeld for "non-hydrogen-like" elements, although having no claim to abs. quant. accuracy, yet leaves little room for doubt of its essential qual. features. The present

paper aims to show that a theory of the complex Zeeman effect is possible which assumes the essential features of Sommerfeld's theory of the at. structure of the elements.

S. C. LIND

The carrying down of polonium with bismuth hydroxide in a sodium carbonate solution. ESCHER. *Compt. rend.* 177, 172-3(1923).—The distribution of Po between the solid and liquid phases is a function of the no. of mols. of Bi and the no. of mols. of Na_2CO_3 contained in a fixed vol. of the mixt.

MARIE FARNSWORTH

Capture and loss of electrons by alpha particles. ERNEST RUTHERFORD. *Proc. Cambridge Phil. Soc.* 21, 504-9(1923).—R. extends some previous investigations by Henderson (*C. A.* 17, 1375) on the charges on the particles in a pencil of α -particles from Ra B and Ra C, using a magnetic field and the method of scintillation counting. He definitely proves the existence of singly charged and neutral α -particles as well as the doubly charged ones usually observed. It is found that in the presence of gas the α -particles gain and lose electrons several times. By changing the gas pressures and counting the scintillations it was possible to measure the mean free path for the gain and subsequent loss of electrons for particles of velocities between $0.94 V_0$ and $0.47 V_0$, where V_0 is the velocity of α -particles from Ra C. The observations indicate a marked difference in the power to gain and hold electrons among different α -particles, though the cause for this is not obvious.

L. B. LOEB

The tracks of alpha particles in a magnetic field. P. KAPITZA. *Proc. Cambridge Phil. Soc.* 21, 511-6(1923).—Using a new and ingenious device for obtaining magnetic fields of 75000 Gauss over a sufficient area for short intervals of time K. studies the curvature of single C. T. R. Wilson α -ray tracks produced by the magnetic field. Segs. out only such tracks as had no bends due to impacts and making use of the curve for the variation of velocity of α -particles near the end of their range given by Blackett, he computes the av. charge on the particles from the curvature of the tracks. In the last cm. of path the particles show an average charge lying between 0.5 and 2 positive units. Each particle has a different variation of charge over its path though each particle changes its charge about a hundred times in a mm. This indicates a marked difference among the α -particles for holding electrons. An explanation is suggested from the fact that Rutherford has found the nucleus of He atoms to be oblate spheroids. If it is supposed that the captured electron describes an orbit about the nucleus whose plane must correspond to some particular plane in the spheroid, then the orientation of the electronic orbit relative to the direction of motion of the α -particle will be fixed for a given particle. Since according to Bohr the orientation of the plane of the orbit relative to its velocity influences the frequency with which the particle may be ionized the phenomenon is accounted for. The difference of the av. charges of the particles means that the particles have different ionizing powers. Thus they must lose energy at different rates. Such difference of energy loss may account for the "struggling" of α -particles observed by Henderson.

R. B. LOEB

Neutralization of hydrogen nuclei in canal rays and the range of α -rays. E. RÜCHARDT. *Z. Physik* 15, 164-71(1923).—The no. of encounters of H nuclei in canal rays with mols. of H_2 , N_2 , and O_2 which result in the addn. of an electron to the H nucleus may be calcd. by assuming that $m v^2/2 \leq (e^2/r)$ and $r \leq r_1$, where m is the mass of the H nucleus; e , the electronic charge; v , the velocity of the canal rays; r , the distance from the nucleus to the electron; and r_1 , the radius of the first orbit or energy level of Bohr's atom. Calcs. based upon the same assumptions satisfactorily account for the range of α -particles. In this case, however, the charge is $2e$ and r_1 is half as large as in the case of the H atom. The crit. velocity of the α -particles from Ra C is given as 6.15×10^8 cm./sec. Addn. of an electron occurs only when the velocity of the α -particle is less than this crit. value.

L. M. HENDERSON

The electron absorbing cross-section of the atom. GREGOR WENTZEL. *Z. Physik* 15, 172-9(1923).—Hund (*C. A.* 17, 2078) has suggested that the electron passes through the central region of the atom, and that the absorbing or scattering part of the atom is of the form of a ring. The inner radius of the ring is very small for swift electrons. This radius increases as the speed of the electron decreases and finally reaches a value equal to the radius of the atom. Then the absorbing ring disappears and the atom is wholly penetrable by very slow electrons. From mathematical considerations of Kulenkampff's data (*C. A.* 17, 1752) on the continuous Röntgen spectra W. endeavors to establish a quant. relationship between the hypothetically introduced inner radius of the ring, the electron speed, and the charge on the nucleus. The expression $1/p = (1/l) + (1/a)$ is deduced in which $a = 1.4 \times 10^{-8}$ cm.; l is defined as the distance from the nucleus at which the potential energy gained (e^2/l) becomes equal to the original kinetic energy of the electron; and p is the inner radius. A qual. relationship

between the inner radius, speed of the electron, and the charge on the nucleus is deduced from the data given by Ramsauer (*C. A.* 15, 3933; 16, 1905) on the absorption of slow cathode rays and from the work of R  chardt (see preceding abstr.) on the neutralization of the charges of canal rays and α -particles.

L. M. HENDERSON

Movements of the earth's surface crust. II. JOHN JOLY. *Phil. Mag.* 46, 170-7 (1923); cf. *C. A.* 17, 2669.—Further development of the theory of the earth's crust as limited by radioactive heat and influenced by isostasy. Not only is continental thickness thus limited but continental area and ocean depths are also detd. by the fact that even if the lighter material forming the constituents had originally, rising like a scum to the surface of the magna, been piled up deeper than at present, they must inevitably have melted away beneath until the present thickness and surface area would be attained.

S. C. LIND

Positive-ray analysis of copper. A. J. DEMPSTER. *Nature* 112, 7(1923).—Rays of Cu were obtained using a Mo furnace. The results indicate 3 isotopes sep'd. by 2 units in the ratios 1.4:1:1, with the lightest isotope strongest, and apparently corresponding to the at. wts. 62, 64, 66. This is the first exception to the previously generally observed rule that elements with odd at. nos. have isotopes with odd at. wts. Two isotopes of Rb were also observed (coming from the furnace cement presumably) with a mean at. wt. of 85.51 as compared with the chem. value of 85.45.

G. L. CLARK

A method of photographing the disintegration of atoms and of testing the stability of atoms by the use of high-speed alpha particles. WM. D. HARKINS AND R. W. RYAN. *Nature* 112, 54-5(1923).—Two photographs of α -particle tracks are reproduced and explained. One shows that the original track splits into 3 branches at the point of collision, one due to the α -particle rebounding at the great angle of 165°, another to the forward track of the nucleus which is hit, and the third to a fragment produced by disintegration of this nucleus. A second photograph shows a new type of secondary track, presumably due to electrons pulled out of the non-nuclear systems of atoms through which the α -particle passes. It is estimated that 10 billion atoms have been shot through with only 3 nuclear collisions in which the initial α -particle has been given a retrograde motion.

G. L. CLARK

Photoelectric effect and the conductivity of crystals. B. GUDDEN AND R. POHL. *Z. Physik* 16, 170-82(1923); cf. *C. A.* 16, 1535, 2806.—The electrons liberated in the interior of a crystal by photoelec. effect move toward the anode and give rise to a current. Its value is increased if the crystal is illuminated also with radiation of long wave length, causing the + charges to be transferred to the cathode—an action which requires hrs. for diamond but only secs. for ZnS. These charges can stay at the electrode surfaces for hours. but under illumination they disappear, giving a reversal of current.

G. R. FONDA

Non-radiating electronic orbits and the normal Zeeman triplet. BRAJENDRANATH CHUCKERBUTTI. *Bull. Calcutta Math. Soc.* 12, 221-4(1922); *Physik. Ber.* 3, 1117 (1922).—A derivation is given for the sepn. of the normal Zeeman triplets. Nothing new is contained.

A. E. STEARN

Discharge in a Lilienfeld tube. O. FRITZ. *Fortschr. Geb. R  ntgenstr.* 29, 228-30 (1922); *Physik. Ber.* 3, 679(1922).—An observation that a change of heat stream of a Lilienfeld tube with inductor and thermoionic valve is followed by a change in the current strength of the tube.

A. E. STEARN

Tube potential and silver bromide darkening. O. FRITZ. *Fortschr. Geb. R  ntgenstr.* 29, 281-96(1922).—As a basis for photographic intensity measurements of R  ntgen radiation F. detd. the milliamp.-sec. product necessary for equal darkening in the case of various tubes as function of the tube potential, which was ascertained by spectrometric measurement of the limiting short wave length of the continuous spectrum. For gas tubes either inductors or high tension rectifiers gave the same results. For Lilienfeld tubes only the latter was used. The darkening effect was about half that of the gas tubes. For both types of tube the photographic activity of the radiation increased approx. as the square of the tube potential.

A. E. STEARN

The milliammeter as measuring device for radiation intensity. O. FRITZ. *Fortschr. Geb. R  ntgenstr.* 29, 223-8(1922); *Physik. Ber.* 3, 679(1922).—For Lilienfeld tubes the proportionality between current and photographically measured intensity is good up to 27 milliamps. both in case of induction coils or high voltage rectifiers. The same holds good for ionization tubes to 21 milliamps.

A. E. STEARN

The energy distribution in the discharge. O. FRITZ. *Fortschr. Geb. R  ntgenstr.* 29, 230-2(1922); *Physik. Ber.* 3, 680(1922).—Spectrographs of the discharge of a R  ntgen tube contg. gas exhibits a peculiar energy distribution (max. and min.), without the ap-

pearance of corrosion or local action on the anti-cathode surface. In this F. seeks to explain his observation of local differences in electron concn. at the cathode. A. E. S.

Paramagnetism and the theory of quanta. PAUL S. EPSTEIN. *Science* 57, 532-3.—The quantum theory of magnetism leads to the conclusion that the magnetic moment of a mol. (m) is equal to jm_0 where m_0 is the "Bohr-magneton" and j is an integer (the "internal quantum number" of the atom). Pauli (*C. A.* 15, 623) has shown that on the basis of the quantum theory Langevin's theory must be replaced by a new one. E. applies these considerations to results recently published by Cabrera (*J. physique* 1921) on the magnetism of salts of metals of the Fe group and obtains values of j which vary from 1 to 5. SAUL DUSHMAN

Progress in the development of theories of para- and of diamagnetism from 1900 to 1920. A. P. WILLS. *Bull. Nat. Research Council* 3, Part 3, 16-112(1922).—These theories are based largely upon the conception of the "magneton," which is "conceived to be a minute aggregate of positive and negative electrons, possessing certain arbitrarily assigned constitutional or structural properties." The most famous theory in this field was suggested by Langevin in 1905. This was subsequently used by Weiss to develop a theory of ferromagnetism. The mathematical theory is discussed in detail by W. As certain deductions of Langevin's theory were found not to be in accord with exptl. results, various attempts were made to modify this theory—notably by Honda, Gans and Oxley. In 1916, Gans proposed a quantum modification of his theory which should apply to all paramagnetic substances at low temps. This theory and modifications suggested by V. Weyssenhoff and Reiche have been found to be successful to a limited extent. Attempts have been made by E. Schroedinger (1912) and H. A. Wilson (1920) to account for diamagnetism in metals as due to the motions of free electrons; conclusions derived are not in good agreement with actual observations. SAUL DUSHMAN

Theories of ferromagnetism—Intrinsic fields. E. M. TERRY. *Bull. Nat. Research Council* 3, Part 3, 113-64(1922).—Langevin's theory of paramagnetism assumes that the state of magnetization depends upon only 2 factors: the external field, which tends to produce alignment of the magnetic elements in the field, and the thermal agitation, which tends to chaotic motion. From this, it follows that the mol. susceptibility (χ_m) varies inversely as the abs. temp. (Curie's law) and that the product $\chi_m T = \sigma_m / 3R$, where σ_m is the magnetic moment per g. mol. at the zero abs. "By postulating a 'mol. field,' Weiss has extended Langevin's theory to ferromagnetic substances. The transition from paramagnetic to ferromagnetic state is explained by assuming that, due to the overlapping of the fields of the individual mols., there comes into existence an internal or mol. field, which added to the external field, accounts for the very large intensity characteristic of this state." This mol. field is very large compared to fields available in the lab. The mathematical argument leads to a modified form of Curie's law, which is in accord with observations on magnetite, pyrrhotite and Fe-Ni alloy. Furthermore, the theory accounts for the increased sp. heat of such substances in the range of temps. where they exhibit ferromagnetism, and also for many of the complicated phenomena of crystals. The hypothesis of mol. fields has also been applied to paramagnetic and diamagnetic substances. Various explanations have been suggested regarding the nature of this mol. field, and the work of Frivold, Gans and Oxley is discussed in detail. SAUL DUSHMAN

Theories of magnetic crystals and the magneton. J. KUNZ. *Bull. Nat. Research Council* 3, Part 3, 165-213(1923).—The phenomena exhibited by crystals of pyrrhotite, magnetite, hematite and certain iron crystals are quite complex. The intrinsic mol. field hypothesis of Weiss (cf. preceding abstr.) has been applied by Weiss, Kunz, Ziegler, K. Honda, Frivold and others to a quant. explanation of these observations. Weiss concluded that the magnetic moment per g. mol. at the abs. zero (σ_m) is always an integral multiple of the elementary unit of magnetic moment (the "magneton"). The no. of magnetons per atom is found to vary widely for different substances (which seems to discredit the whole theory). Furthermore, on the basis of Bohr's theory the magnetic moment of an electron revolving about a nucleus of unit charge (H atom) is found to be 5 times larger than Weiss' magneton. Brief mention is also made by K. of Parson's magneton theory of at. structure. SAUL DUSHMAN

Magnetic theories prior to the discovery of the electron. S. L. QUIMBY. *Bull. Nat. Research Council* 3, Part 3, 3-15(1922).—A review of the theories of Poisson, Ampere, Weber and Ewing. SAUL DUSHMAN

The angular momentum of the elementary magnet. S. J. BARNETT. *Bull. Nat. Research Council* 3, Part 3, 235-250(1922).—"If the magneton has angular momentum, it must exhibit the dynamical properties of a gyroscope." Consequently if a ferro-

magnetic substance is rotated, each elementary magnet will contribute a minute magnetic moment parallel to the axis of the impressed rotation and the originally unmagnetized body must have become magnetized along the axis of rotation. The mathematical theory leads to a relation between the magnetic intensity and the ratio e/m of the charge to the mass of the electron. The expts. of Barnett and those of Einstein and de Haas are discussed. These have shown that in ferromagnetic substances there exist electronic currents of electricity in orbital revolution or rotation, and that the magnitude of e/m is the same as that of the electron.

SAUL DUSHMAN

Magnetostriction and its bearings on magnetic theories. S. R. WILLIAMS. *Bull. Nat. Research Council* 3, Part 3, 214-224(1922).—In general, a magnetic field causes a change in dimensions of ferromagnetic substances while reciprocally mech. deformations produce changes in the magnetic properties. All such phenomena are classified under the title of magnetostriction. An excellent review is given of the extremely numerous observations in this field.

SAUL DUSHMAN

Theories of magnetostriction. S. L. QUIMBY. *Bull. Nat. Research Council* 3, Part 3, 225-34(1922).—A mathematical discussion of the theories of Maxwell, Von Helmholtz, Larmor and J. J. Thomson.

SAUL DUSHMAN

The motion of electrons in gases. V. A. BAILEY. *Phil. Mag.* 46, 213-8(1923).—B. makes a critical analysis of the methods of detg. the velocity of electrons in gases at various pressures and under different voltages. He points out that the velocity W is not universally proportional to X/p (where X is the voltage drop and p the pressure). Diffusion is also a factor which may not be neglected, and which renders some of the mobility methods inapplicable under some conditions. While recognizing that the attachment of free electrons to form negative ions does, as is generally held, depend on X/p , the nature of the gas and its state of dryness, B. points out the unsuitability of the exptl. methods employed to det. the factor (h) of the probability of electronic attachment. B. regards the result for (h) as especially doubtful for low values of X/p .

S. C. LIND

The theory of the abnormal cathode fall. F. W. ASTON. *Phil. Mag.* 46, 211-13(1923).—A criticism of the theory of Ryde (*C. A.* 17, 3670) to explain the abnormal cathode fall or dark space. A. presents reasons for doubting R.'s theory and cites his own earlier efforts, neither of which appears adequate as an explanation. A. predicts that the true explanation will probably be found in the neutralization or reversal of the polarity in positive ions as they progress through the field.

S. C. LIND

The emission of secondary electrons from metals under electronic bombardment. FRANK HORTON AND ANN C. DAVIES. *Phil. Mag.* 46, 129-35(1923).—Reply to criticisms of Gill (*C. A.* 17, 2387).

S. C. L.

The scattering of electrons by aluminium. C. DAVISSON AND C. H. KUNSMAN. *Phys. Rev.* 19, 534-5(1922).—Observations similar to those made on Ni (cf. *C. A.* 16, 379) have now been made on the scattering of electrons by Al. For bombarding potentials up to 200 v. the max. intensity of scattering is back along the path of the primary beam and the distribution is represented by a formula. Analysis of the distribution indicates that the L electrons in the Al atom are at a distance of about 3×10^{-9} cm. from the nucleus.

W. F. MEGGERS

A quantitative relation in normal cathode fall of glow discharges. HERMAN SCHÜLER. *Physik. Z.* 24, 259-61(1923).—When the no. of volts expressing the normal cathode fall of glow discharges in H_2 are plotted on a linear scale the values appear to cluster at regular intervals sepd. by 16.4 v., the ionization potential of H_2 . This regularity characterizes elements in the first 3 columns of the periodic system. A similar regularity is found among elements of the higher groups except that for these the periodicity is close to 13.53 v., the ionization potential for the H atom. No discussion of the phys. processes underlying these regularities is attempted.

W. F. MEGGERS

Photoelectric currents of a hundred amperes? WALTER DÖLLENBACH AND GERHARD JAHN. *Physik. Z.* 24, 265-9(1923).—Exptl. facts and explanations are presented to cast doubt on the claim of Schenkel and Schottky that they measured photoelec. currents up to 100 amps. in large Hg-vapor rectifiers.

W. F. MEGGERS

Temperature, light and electron emission of tungsten wires heated by alternating current. HERMANN HUNKEL. *Physik. Z.* 24, 252-7(1923).—Very few investigations have been made on the temp. of wires carrying a. c. This problem has recently become of interest and practical significance in connection with work on light-telephony and the development of cathode tubes heated by a. c. Instead of using the relatively insensitive method of detg. the course of temp. from resistance variations in wires, in the present work this is detd. from the course of the emission of light and electrons. The temp. curves obtained quite independently from either the electron-emission or

the light-emission curves are identical; they are essentially sine waves lagging in phase almost exactly $\pi/4$ behind the curve of the heating current. Tungsten wires 0.01, 0.02 and 0.03 mm. were studied with heating-current frequencies of 35, 50 and 75 cycles. These variables, under the exptl. conditions, had no appreciable effect on the phase angle. This report is an ext. from a Göttingen dissertation. W. F. MEGGERS

The secondary rays produced in a gas by X-rays. PIERRE AUGER. *Compt. rend.* 177, 169-72(1923).—The method of C. T. R. Wilson is used. In addition to the secondary electron, in A, Cl and I, but not in N₂, there is a tertiary electron with a much shorter path, going in the opposite direction. The life of the tertiary β -ray depends on the nature of the atom and not on the frequency of the X-ray. The emission of the secondary electron is accompanied by the emission of a quantum of energy. When this energy is absorbed by the same atom, a tertiary electron results. In the case of I, the process is repeated and a quaternary electron results. MARIE FARNSWORTH

A suggestion of the characterization of Röntgen rays. K. STAUNIG. *Fortschr. Geb. Röntgenstr.* 29m, 212-5(1922); *Physik. Ber.* 3, 679(1922).—Through the theoretical work of March and the exptl. data of Fritz, the distribution of intensity in a continuous spectrum is unequivocally fixed when the limiting short wave length λ_{min} is fixed. It is proposed, for medical purposes, to characterize each ray in terms of λ_{min} in order to create an absolute measure of hardness. By adding focal distance and the milliamp.-seconds the radiation from tubes with like anticathodes is qual. and quant. defined. A. E. STEARN

The limits of K absorption (of X-rays) of certain elements. J. CABRERA. *Anales soc. españ. fis. quim.* 21, 245-52(1923); cf. C. A. 17, 2080.—The work of other investigators is discussed. In the expts. made by C. the values obtained agreed with those published by other workers. L. E. GILSON

The relative intensities of X-ray lines. F. C. HOYT. *Phil. Mag.* 46, 135-46(1923).—Bohr's correspondence principle furnishes a method of estg. the relative frequencies of occurrence of different quantum transitions, but does not give an expression for the intensity of a given line. On the basis of Bohr's at. constitution calcu. is made of the relative intensities of the K series lines for Rh in 6 different ways. The procedure adopted has promise. By comparison with exptl. results 3 of the methods can be discarded. No sharp distinction can be made between the other 3. S. C. LIND

A spectrographic study of ultra-violet fluorescence excited by X-rays. J. O. PERKINS. *Phys. Rev.* 19, 538-9(1922).—In the phenomenon of fluorescence, the emitted radiation has a greater wave length than the exciting radiation. Therefore, with X-rays as the incident radiation it is not unlikely that fluorescence in the ultra-violet region would result. With this idea as a working basis, a large no. of substances were subjected to X-rays and with the aid of an ultra-violet spectrograph, the photographic plate recorded whatever ultra-violet fluorescence there might be. Fourteen samples of the double salts of U, 23 oxides and 54 samples of miscellaneous salts gave negative results. Exposures varying from $1/2$ to 15 hrs. were made with a Coolidge tube operating at 2 milliamp., 50,000 v. The chlorides of K, Li, Rb, Na, and Cs gave positive results. NaCl has a very strong band at a wave length 2,470 Å. CsCl gave the best results with a strong band extending from 5,720 to 2,340 Å. with 3 points of max. intensity. W. F. MEGGERS

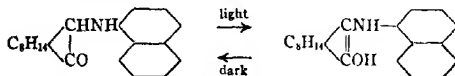
The penetration of cathode rays in molybdenum, and its effect on the X-ray spectrum. D. L. WEBSTER. *Phys. Rev.* 19, 545-6(1922).—The penetration of cathode rays in Mo was investigated by studying the emission spectrum around the K absorption limit. The stronger absorption on the short-wave side of this limit reduces the emission intensity by about 9% at 25 kv. and about 16% at 70 kv., when the cathode rays go in at about 45° to the surface and the X-rays emerge at the same angle. As no rays of this wave length are produced by electrons of less than 20 kv. energy, the 8% at 25 kv. may be due largely to surface irregularities, which must be of the order of a μ . The increase at higher voltages measures the av. depth of penetration of the cathode rays, which runs up to about 2 μ or so at 70 kv. W. F. MEGGERS

The light emission under the action of molecular electric forces on the surfaces of crystals. BRUNO SAXEN. *Acta Academiae Aboensis Math. Phys.* I, 5, 16; *Chem. Zentr.* 1922, III, 314-5.—Elec. fields are probably present on the surfaces of solids such as crystals. Stark has considered it possible (Nobel lecture, *Änderungen der Struktur und des Spektrums chemischer Atome*) that the appearance of such mol. elec. effects has an influence on spectral lines, which are emitted directly on the surface. To prove this supposition a very intensive light emission must be incited on the surface and care must be taken that only a very thin layer of light be visible. Canal rays are therefore used for inciting the light. Two effects are produced, the sepn. of atoms from

the surface and the emission of light by these liberated atoms, which show their max. light directly on the surface. A special contrivance is used to utilize only that layer of light directly on the surface. As surfaces fluorspar and rock salt, which emit a continuous spectrum in the ultra-violet, are used. Lines of canal rays and of metal atoms which have been sep'd. from the surface by the canal rays are emitted in a layer directly on the crystal surface so that the layer appears to belong partly to the solid, partly to the surrounding gas. Emerging from this layer they appear diffused if the effect of the elec. field is great, but sharp if this effect is small. From this conformity of the diffusion of the elec. effect it is concluded that the diffusion is caused by mol. elec. forces of the crystal.

C. C. DAVIS

Phototropism in solution. I. B. K. SINGH AND DALIP SINGH. *Proc. 7th Indian Sci. Cong.* 1921, Ixxv.—A reversible isomeric change produced by light and accompanied by color changes has hitherto been observed only in solid substances. Comps. are described which exhibit *phototropism in soln.* but not in the solid state. CHCl_3 solns. of α -naphthylaminocamphor, *ar*-tetrahydro- α -naphthylaminocamphor and *m*-phenylene-bisaminocamphor are colorless, but on exposure to sunlight become bottle-green. This change occurs in approx. 1 min. for the first 2 comps., and in 15 min. for the third. In each case the color vanishes when the green solns. are kept in the dark 24 hrs. The suggestion of Senier and Sheppard (cf. *C. A.* 4, 1025) that phototropism is not due to intramol. change but to reversible mol. rearrangement of the mols. into mol. aggregates must therefore be revised. The change in color is probably due to a change in the chem. structure of the mol., thus:



C. C. DAVIS

Improvements of standard spectrometric methods. O. FRITZ. *Fortschr. Geb. Röntgenstr.* 29, 213-23(1922); *Physik. Ber.* 3, 679(1922).—For establishing a generally valid exposition table for Röntgen reception it is necessary for each thickness of object to det. λ_{min} and the milliamp.-sec. product. All other factors being the same, a gas contg. tube gives about twice the intensity given by a Lilliefeld tube. Tables are given for both tubes which give λ_{min} and milliamp.-secs. as function of thickness of object for various kinds of objects. These tables will hold fairly well for Coolidge tubes as the intensity of the Coolidge tube to a gas contg. tube under like conditions is 1:1.9.

A. E. STEARN

Homogenizing the discharge of a Lilliefeld tube. O. FRITZ. *Fortschr. Geb. Röntgenstr.* 29, 233-6(1922); *Physik. Ber.* 3, 680(1922).—The object of the work was to det. whether the high resistance placed by Lilliefeld between the glowing cathode and the working cathode was effective in rendering the radiation homogeneous. He found upon introducing equal tensions in equal times with equal milliamp. nos., the same darkening of a photographic plate, and concluded that the interpolation of this resistance has no effect on the quality of the radiation, that is, no real homogenizing effect was noted. On the contrary there was a shift in the value of λ_{min} to shorter length.

A. E. STEARN

The production of series in the gold arc spectrum. V. THORSEN. *Naturwissenschaften* 11, 500-1(1923).—To overcome the relatively weak intensity of the Cu lines, photographs of the Au spectrum were taken with a quartz prism spectrograph. Numerous new lines are tabulated which were obtained by this method.

C. C. DAVIS

The fine structure of a certain class of band spectra. A. KRATZER. *Ann. Physik* 71, 72-103(1923).—The mutual influence of mol. rotation and electronic motion is calcd. for the special case that the resultant electronic angular momentum, p_e , has the same axis as the total angular momentum, p . (The more general case where p_e makes an angle with p will be treated later.) This leads to the spectral term $\approx 2\delta(m \neq \epsilon) + (m \neq \epsilon)^2 B^* - B^* m^2 (m \neq \epsilon)^2 \dots$, corresponding to the rotation of the mol. Here δ , ϵ , B , and μ are const., for a given band; m is the rotational quantum no.; ϵ is $2\pi p_e / h$, and is virtually an electronic quantum no., although not necessarily an integer; ϵ may be positive or negative, according to the direction of p_e with respect to p . Application of the correspondence principle shows that in general the changes $\Delta m = \pm 1$ or 0 are possible, but that in some cases only ± 1 or even only $+1$ or -1 may be possible. K. shows that the fine structure of the violet cyanogen bands, including the perturbations, can be satisfactorily explained in terms of the above equation, applying it to both initial and final states of the emitting mol. For both states, $\epsilon = 1/2$. The

bands have a real doublet structure which however differs from the apparent doublet structure. The difficulty formerly existing with respect to the single missing line in the center of the band is now removed, and it is now possible to assume that all lines for which $m = 0$ in either the initial or final state are missing. This assumption and the above equation are conclusively verified by the fine structure of the Zn, Cd, and Hg bands. (In regard to the CN bands, cf. also Kratzer, *Sitzungsber. der Bayerischen Akad. der Wiss.*, 1922, p. 107; and *C. A.* 17, 1538 in regard to the others.) Values of ϵ of $1/2$, $1/4$, and 0 occur in the terms of the various bands, so that it appears that the angular momentum of the electronic motion can be represented by rational multiples of $h/2\pi$. When $\Delta m = 0$, it is found that ϵ changes sign in passing from the initial to the final state; for $\Delta m = \pm 1$, there is no change of sign of ϵ . Probable values of the vibrational quantum no. are assigned to the various bands. It is concluded from the very small moment of inertia (only $1/2$ that of N_2), as detd. from the constant B , that the Zn, Cd, and Hg bands are really due to hydrides of these elements.

R. S. MULLIKEN

The absorption spectra in the ultra-violet of the alkaloids of the isoquinoline group.

Narceine. PIERRE STREINER. *Compt. rend.* 176, 1379-81(1923).—A study of the ultra violet spectra of narceine in EtOH, employing the quant. method of V. Henri. The depression in the curve of Dobbie and Lauder (1903, no reference) is shown to correspond to a broad absorption band, with a max. wave length of approx. 2707 Å, and a coeff. of absorption approx. 9800 and a min. of 2539 Å. and 8000, resp. Absorption curves (frequencies as abscissae, logarithms of the coeffs. of absorption as ordinates) are shown for narceine and for narcotine in EtOH, opianic acid in Et₂O-EtOH and hydrocotarnine in hexane (cf. *C. A.* 17, 2832). The curve of narceine is in general similar to those of narcotine and opianic acid, the band of narceine being displaced towards the short wave lengths by approx. 330 Å. compared to narcotine and approx. 100 Å. compared to opianic acid. By this method 0.05 mg. of narceine in 2 cc. of solvent can be detd. spectrographically.

C. C. DAVIS

Diffraction by molecular clusters and the quantum structure of light. C. V. RAMAN. *Nature* 109, 444-5(1922).—It has been observed that the Einstein-Smoluchowski formula for the scattering of light by a fluid is approx. valid in the case of liquid CO₂ and vapor for a range of only a few degrees below the crit. temp., and then falls off much more rapidly than according to the formula. Since the latter is based on the classical electromagnetic theory, R. advances the view that the discrepancy may have to be accounted for by assuming "a quantum theory of the structure of light as propagated in space (and not only when it is absorbed or emitted)." SAUL DUSELMAN

Magneto-optics. L. R. INGERSOLL. *Bull. Nat. Research Council* 3, Part 3, 251-61(1922).—The magneto-optical phenomena include the 3 classes known, resp., as the Faraday, Kerr and Zeeman effects. The phenomena are described briefly and a summary is given of the theoretical work in this field. SAUL DUSELMAN

Infra-red spectra. (I) **Infra-red emission spectra of various substances, and (II) infra-red absorption spectra of benzene and some of its compounds.** J. E. PURVIS. *Proc. Cambridge Phil. Soc.* 21, 556-65(1923).—Curves are given for the emission spectra of a Nernst filament, Welsbach burner, fish tail burner, Bunsen burner, acetylene jet and CO jet. The transmission curves of liquid C₆H₆I are compared with curves previously detd. for C₆H₅Br and C₆H₆. While the general form of the curves is the same, the bands shift toward the visible end of the spectrum in the case of C₆H₆I. The transmission through vapor of C₆H₅I, C₆H₅Br, C₆H₅Cl, C₆H₆ was also studied between μ 1 and μ 3. Liquid C₆H₆ shows 3 bands at μ 1.7, μ 2.08 and μ 2.49. These, especially the one at μ 1.7, show signs of division when the radiations pass through vapor. The curves of C₆H₅Br, C₆H₅Cl and C₆H₆I also show signs of division. The liquid band of C₆H₆ between μ 3 and μ 4 (Coblentz), and the absorption of the vapor in the same region are compared. The liquid band seems to be the result of sep. bands crushed together.

ROGER G. FRANKLIN

The absorption of the ultra-violet rays by phosphorus and some of its compounds. J. E. PURVIS. *Trans. Cambridge Phil. Soc.* 21, 566-7(1923).—In dil. soln. P(C₆H₅)₃ shows a wide weak band and great general absorption. The vapor at 140° and 740 mm. showed a weak band between λ 2500 and λ 2300. P vapor shows no absorption bands. General absorption begins around λ 2100 at 70° and begins at higher values of λ with increasing temp. PH₃ shows no absorption bands. At temps. between 30° and 100° the rays are transmitted to about λ 2200.

ROGER G. FRANKLIN

A method for distinguishing the so-called arc lines from the spark lines of the spectrum. W. WIERN. *Münchn. Ber.* 1922, 119-20; *Physik. Ber.* 3, 1181(1922); cf. *C. A.* 17, 1381.

A. E. STERN

Structure of the spectrum of the neutral chromium atom. MIGUEL A. CATALÁN. *Anales soc. españ. fis. quim.* 21, 84-125(1923).—The arc and spark spectra of Cr are composed of 2 classes of lines, those of the neutral atom and those attributed to the ionized atom. The lines of the first class group themselves in several series of triplets which follow Rydberg's formula. Twelve multi-triplets are also present. The diffuse triplets resemble those of Mn. Complete data on all these lines are given. The potential of ionization of Cr was calcd. to be 6.7 v. The primary potential of resonance calcd. from the triplet λ 4254, 4275, 4290, is 2.89 v. L. E. GILSON

Structure of the spectra of the neutral chromium and molybdenum atoms. MIGUEL A. CATALÁN. *Anales soc. españ. fis. quim.* 21, 213-36(1923).—C.'s work on Cr is reviewed (cf. preceding abstr.). The spectrum of Mo is of the same type as that of Cr. Extensive numerical data are given. The potential of ionization of Mo was calcd. to be 7.1 v. The primary potential of resonance calcd. from the triplet λ 3798, 3861, 3904, is 3.2 v. L. E. GILSON

Radiation equilibrium. E. A. MILNE. *Monthly Not.* 81, 510-15; *Chem. Zentr* 1922, III, 1076.—Since at radiation equil. of a gas the emitted energy is equal to the absorbed energy, the emission spectrum of a gas absorbing a wave length must have a different energy distribution from a non-absorbing gas. Calcns. are given for a special astrophys. problem. C. C. DAVIS

The absorption produced by electrically luminous sodium vapor. F. H. NEWMAN. *Phil. Mag.* 46, 22-9(1923).—A study of the intensities of the D and E lines of Na vapors under low-voltage arc discharge as influenced by self-reversal, current density, and other factors. A Na-K alloy was used in some expts. The lines of K were faint under all conditions compared with those of Na, but became relatively brighter as the p.d. was decreased. A constriction at one end of the discharge tube and quartz windows at the constriction and in the wider portions enabled observation to be made under varied conditions. S. C. LIND

The auroral spectrum and the upper strata of the atmosphere. L. VEGARD. *Phil. Mag.* 46, 193-211(1923).—V. continues his studies of the spectrum of the northern lights (C. A. 15, 2778). These spectra have a possible two-fold interest in disclosing the nature of the gases constituting the upper atm. in which the spectrum is produced, and of the cosmic radiation producing it. One quartz and two glass spectrographs were used. Of the 35 lines observed in exposures as long as 18 hrs. all but 4 have been positively identified as N lines. By a process of elimination, involving extensive consideration of the probable temp. distribution and of the possible condens. of H, He, and N at heights from 100 to 300 km., it is concluded that the remaining 4 lines are also N lines which are not readily reproducible under other conditions. No evidence for geocoronium was obtained. It is considered more probable that electrons constitute the corpuscular rays and that an electrically charged upper layer appears probable. S. C. LIND

Line structure and atomic structure. NIELS BOHR. *Ann. Physik* 71, 228-88 (1923).—A general review of the present state of the quantum theory of at. structure based on the series relationships existing in the line spectra of the elements. C. C. KIESS

Regularities in the arc spectrum of titanium. C. C. KIESS AND HARRIETT K. KIESS. *J. Wash. Acad. Sci.* 13, 270-5(1923).—Many of the lines of the arc spectrum of Ti assigned by King to temp. classes I and II have been linked together in groups known as multiplets on the basis of recurring const. wave-number differences. Groups of 6 and 7 lines are characterized by the differences 170.0 and 215.8, while in groups of 11 and 13 lines exist the differences 42.0, 62.2, 81.7, and 100.2. The *raies ultimes* of Ti belong to a 13-line group. C. C. KIESS

The spectrum of ammonia. W. B. BRIMMER. *Proc. Roy. Soc. London* 103A, 696-705(1922).—Observations have been made of the spectrum of NH_3 excited under a variety of exptl. conditions. The 2 bands in the greenish yellow probably originate in the normal NH_3 mol. and remain unresolved even under high dispersion. The ultraviolet band previously measured by Fowler and Gregory emanates from a more stable compd. of N and H. The α -band of Eder and Valenta probably originates in a compd. of N and H of intermediate stability and is of very complex structure consisting of about 3000 lines. Of these about 300 of the brightest between 4247 Å. and 6437 Å. have been measured with an accuracy of 0.01 Å., and the resulting wave lengths have been compared with lines in the solar spectrum. There is no conclusive evidence that the α -band occurs in the spectra of the sun and sun-spots. C. C. KIESS

The spectrum of fluorine. H. G. GALE. *Phys. Rev.* 19, 530(1922).—The spectrum of F was studied at atm. and at reduced pressures. The gas was contained in a

bulb having a fluorite window through which the spectrum was photographed with a concave grating of 1.5 m. radius. In the interval 3470 to 7800 Å., 52 lines were measured, 7 longer than 7400 Å. being new. With a powerful spark, 15 additional lines appeared in the orange and red.

W. F. MEGGERS
 The absorption spectra of chloroform in the near infra-red. J. W. ELLIS. *Phys. Rev.* 19, 546(1922).—To study the region 1.0 μ to 2.8 μ an auto-collimating spectrograph was constructed with two 30° medium flint glass prisms through which the radiation from a 108-watt W lamp passed twice. A Bi-Ag thermocouple and a Leeds-Northrup movable coil galvanometer were used. Readings were taken as the radiation passed alternately through an empty glass cell in front of a 0.5 mm. slit and a similar cell of 3 mm. thickness filled with CHCl₃. Five distinct bands were observed with maxima and percentages of absorption as follows: 1.140 μ , 10%; 1.385 μ , 16%; 1.660 μ , 56%; 1.835 μ , 35%; 2.425 μ , 88%.

W. F. MEGGERS
 The absorption spectrum of colloidal arsenious sulfide. A. BOUTARIC AND M. VUILLAUME. *Compt. rend.* 177, 250-61(1923).—The absorption spectrum of colloidal As₂S₃ is studied by means of the Fery spectrophotometer. In this app. the displacement of the absorbing prism which, for any particular radiation λ , compensates the absorption of the medium under examn. gives $\log I_0/I$ where I_0 designates the initial intensity of the incident radiation λ and I the intensity of this radiation after it has traversed the absorbing medium. If colloidal As₂S₃ behaved as a turbid medium one should have (1), in the case where the particles in suspension are small compared with λ , $\log I_0/I$ varying inversely as the fourth power of λ (Rayleigh's law), (2) in the case of larger particles $\log I_0/I$ varying inversely as some power n of λ , n being less than 4 and correspondingly less as the particles are greater. The absorption curve of a sol of 0.2 g. per l., however, does not follow either of these laws but shows a regular increase in n from $n = 3.3$ for λ 6100 to $n = 12$ for λ 5300, with $n = 4$ at about λ 6200. The absorption of a colloid of As₂S₃ may then be the resultant of two phenomena: (1) an absorption by diffusion obeying Rayleigh's law, (2) a selective absorption on either side of λ 6200. The selective absorption may occur at reflection of the rays incident on the surfaces of the granules; it must vary in the same sense as the total surface area of these granules and therefore diminish when the number of particles decreases by gaining in size. It is verified that a modification which increases the size of the particles (e. g., prolonged boiling) decreases the selective absorption.

W. F. MEGGERS
 A method for observing weak absorption lines. E. MADELUNG AND R. GÖTZE. *Physik. Z.* 24, 257-9(1923).—A very narrow absorption line or one in which only slight darkening occurs is difficult to observe and ordinarily requires either spectroscopes of very high resolving power or very sensitive photometric methods. An interferometer method which reverses the absorption spectrum in such a way as to cause the absorption lines to appear as bright lines on a dark background is proposed for more favorable observation of weak absorption lines. A modified Jamin interferometer which is completely sym. and cheaper in construction than the Michelson instrument is described.

W. F. MEGGERS

Importance of the physics of incommensurable particles in physical investigations (FREUNDLICH) 2.

4—ELECTROCHEMISTRY

COLIN G. FINK

Electrical smelting of brass. R. JULLUM. *Teknisk Ukeblad* 39, 223(1921).—A thorough consideration of the subject. The furnace service is very simple and does not depend so much on trained people. The labor conditions are considerably better than for fuel-fired furnaces. The working is more cleanly as there is no transport or handling of fuels. A great saving is due to the reduced metal losses. Various authors indicate this to vary from 0.15 to 1.5% by elec. smelting, mostly below 1%. This is due to the following facts: Only small amts. of air come into contact with the melted metal and it is possible to maintain a deoxidizing atm. over the bath. The reduction of the time required for the smelting and discharging also reduces losses. Owing to the high efficiency of the elec. heating, the power costs usually do not much exceed the fuel costs of other furnaces. A great advantage is the possibility of obtaining a high-grade product without using crucibles. The elec. furnaces can be kept practically free from O₂ and other injurious gases and so the metal obtained is less porous and bladdery and accordingly the % of discards is reduced. Finally a series of furnace

types are mentioned, some of them illus. by drawings or photos: (1) Baily's resistor furnace, (2) General Elec. Co.'s smothered arc furnace, (3) Schlegell's furnace, (4) Rennerfelt's, (5) Booth's rotary, (6) Detroit rocking, (7) Week's, rocking or rotary, (8) Moore's revolving, and (9) Ajax-Wyatt induction furnace. C. H. A. S.

An improvement in electrolytic silver refining. A. H. W. CLEAVE. *Eng. Mining J.-Press* 116, 21-2(1923).—The newly developed cells are circular, 36 in. in diam., and the cathodes rotate at a peripheral speed of 40 ft. per min. The c. d. may be from 75 to 150 amp. per sq. ft. The electrolyte is contained in the annular space between the outer and inner walls of the cells. This space is 8 in. wide and 18 in. deep. By means of the specially designed cathode, and multiple grouping of the anodes, the current becomes a pulsating one, which causes the deposited Ag to adhere loosely to the cathode so that it is easily removed by a rubber scraper. The cathodes will last indefinitely, and when once started, the cells require no attention other than the occasional removal of the fine silver from the collecting trays, and the renewal of the anodes. Though the anodes contain from 10 to 16% of base metals the deposited Ag is from 999 to 999.9 fine. C. C. VAN VOORHIS

Heat losses and chemical action in the high-voltage, high-frequency discharge through air. FARRINGTON DANIELS, PAUL KERNE AND P. D. V. MANNING. *Trans. Am. Electrochem. Soc.* 44, (preprint)(1923).—A discharge was produced by a Tesla coil at about 100,000 v., in a large chamber constructed from a terra-cotta sewer pipe. A central wire 91.5 cm. long and a wire screen 41 cm. in diam. formed the electrodes. Outside of the netting was a large cylinder of paraffined paper, and the whole chamber was arranged to function as a calorimeter. The air was analyzed for O₂ and nitric acid. There is no advantage in discharges of this type for fixing N. The "cold" discharges waste just as much electrical energy in the form of heat, as do the arcs, the only difference being that the consumption of elec. energy is small and so the temp. rise is less. Short exposures to the elec. discharge gave a higher chem. efficiency than long ones. The ratio of O₂ to nitric acid varied from 16 to 2.4. This ratio depended chiefly on the character of the discharge. The more intense the pink streamers the more nitric acid was produced. The more uniform the blue corona the greater was the proportion of O₂. Sparking destroyed O₂ and did not greatly increase the yield of nitric acid. Approx. 45% of the total energy supplied to an oscillation circuit of the Tesla type was evolved as heat in a large discharge chamber contg. air. Approx. 1% of the total energy was used in chem. action. Of the energy actually supplied to the discharge chamber about 2% was converted into chem. energy and 98% into heat. This chem. efficiency is of the same order of magnitude as that obtained in arcs and in other types of corona discharges in air. It is significant that in spite of the large no. of expts. on the passage of electricity through air in various types of app. and under radically different conditions the max. chem. efficiency remains limited to a few %. C. G. F.

Composition and aging of insulating varnishes. H. C. P. WEBER. *Trans. Am. Electrochem. Soc.* 44, (preprint)(1923).—During the drying and oxidation of varnishes, conducting materials are formed which produce appreciable lowering of the insulation resistance of elec. app. Values are given to show that the amt. of these "low resistance materials" is proportional to the amt. of oil in the varnish, and that there is a noticeable difference in the amt. produced by different oils. The amt. of acidity formed is really a function of the time, increasing as the oxidation progresses. For most varnishes the oxidation increases up to 96 hrs., but after that it is practically complete, when the film is thin. The values are really characteristic for the particular varnish. While the quantity increases with time, the order of the different samples remains essentially the same so that for purposes of comparison a 48-hr. test period is as good as a 96-hr. period. Linseed oil varnishes are the most acid; china wood oil varnishes develop less acidity. With the same oil the acidity developed is greater the greater the percentage of oil in the varnish. C. G. F.

Simple regenerating vacuum device (WARAN) 1. Electrolytic oxidation and reduction phenomena in organic chemistry (LÉMARCHANTS) 10.

Primary electric battery. H. WILHELM. U. S. 1,464,838, Aug. 14. An electrolyte, which may contain ZnCl₂, NH₄Cl, potato flour and H₂O, is allowed to gelatinize in a Zn receptacle and a cartridge comprising a C stick is then inserted into the gelatinized material.

Storage battery plate. J. BARNA. U. S. 1,463,788, Aug. 7. Structural features.

Storage battery separators. L. N. BENT. U. S. 1,463,864, Aug. 7. Nitrocellulose is mixed with camphor or other latent solvent, an active solvent such as alc. and an

ingredient, *e. g.*, Na_2SO_4 or other non-injurious material which is partially removed by warm H_2O or other solvent (which does not dissolve celluloid) after the material is formed into thin sheets.

Electrolyte-level indicator for storage batteries. R. SIMPSON. U. S. 1,464,516, Aug. 14.

Dry-cell electric battery. W. S. DOE. U. S. 1,464,413, Aug. 7. Structural features.

Electrodes. S. R. ILLINGWORTH. Brit. 191,827, Oct. 18, 1921. Electrodes, particularly those for use in furnaces, are manufd. from the substances varying from smokeless fuel to true coke set out below, by compressing one or other of them, heating it to at least $50\text{--}100^\circ$ above the temp. of decompn. of resinic matter in the compressed substance, and preferably to 600° , and then impregnating it with pitch rendered liquid by heat and carbonizing at $800\text{--}1000^\circ$ or upwards. The substances used are (a) coals preheated below 600° as described in 164,104 (C. A. 16, 1312) and 175,888 (C. A. 16, 2217), or coals preheated above 600° as described in 186,384 (C. A. 17, 336), (b) coals oxidized as described in 186,085 (C. A. 17, 336), (c) coals blended as described in 186,085 (C. A. 17, 336), (d) coals low in volatile matter as described in 187,328 (C. A. 17, 1132), (e) carbonized coking coals of high O content (over 8%) which, when carbonized at temps. of $50\text{--}100^\circ$, or higher, above the temp. of decompn., give a hard fuel of dense structure, and (f) carbonized bituminous coals whose resinic content is reduced below 5% and which produce a coherent product when carbonized at 500° . A suitable construction is specified.

Manufacture of carbon electrodes. I. SZARYASY. Can. 233,714, Aug. 21, 1923. CH_4 is decomposed in an externally heated chamber to produce a mixt. of soot and tarry substances which is made into electrodes.

Apparatus for electrolysis of water. W. G. ALLAN. U. S. 1,464,840, Aug. 14.

Cell for electrolysis of water. W. G. ALLAN. U. S. 1,464,689, Aug. 14. Structural features.

Electrolyzing alkali halides. K. OCHS. Can. 233,756, Aug. 21, 1923. In the electrolysis of alkali halides a horizontal diaphragm is used and the gas formed in the anode space is maintained under a reduced pressure to give the desired velocity of filtration of the electrolyte.

Apparatus for the electrolysis of alkali chlorides. K. OCHS. Can. 233,755, Aug. 21, 1923. The usual layer of BaSO_4 and asbestos used in app. for electrolyzing alkali chlorides is substituted by subdivisions or vertical partitions which give easier passage to the current.

Apparatus for the electrolysis of metals. A. CREMER. Can. 233,059, July 31, 1923.

Wire electrode for electrolysis. M. HUTH. Can. 233,757, Aug. 21, 1923. The electrode consists of wires connected with one and the same weighting piece or each wire may be suspended from a common conductor and have a weighting piece on each end.

Electrolyte for deposition of zinc. C. BIANCO. Brit. 192,041, Nov. 16, 1922. An electrolyte for depositing Zn contains H_2SO_4 , ZnO in excess of the quantity necessary to neutralize the acid so that part remains in suspension, and boric acid. The compn. preferred comprises 250-350 parts ZnO, 10-25 parts alum, 6-20 parts boric acid, 5-25 parts FeSO_4 , 10-25 parts Na_2SO_4 , 75-100 parts H_2SO_4 , and 644-455 parts H_2O .

Electrolyte for aluminium production. A. PACZ. U. S. 1,464,625, Aug. 14. An electrolyte is prepd. by reacting with Al at a temp. above its m. p. upon a double fluoride of Na and Si, *e. g.*, Na_2SiF_6 .

Recovery of tin-plate scrap. R. A. HOLLAND. Can. 233,677, Aug. 21, 1923. Tin plate is immersed in an electrolyte in elec. association with an element electronegative thereto having a depolarizing substance in contact therewith. The galvanic action causes the Sn to dissolve and it is recovered by electrolysis. App. is also specified.

Separating from a mixture, one or more suspension colloids, true colloids, ions or dissolved substances. B. SCHWERIN. Can. 233,735, Aug. 21, 1923. The mixt. is disposed between 2 electrodes so that it is sepd. therefrom by 2 diaphragms acting electro-osmotically and having different potential characters dependent upon the constituents to be sepd. and an elec. current is passed from one electrode to the other through the diaphragms and the mixt.

Apparatus for extracting liquid from suspensions. B. SCHWERIN. Can. 233,736, Aug. 21, 1923. A perforated and a non-perforated electrode are located in each chamber of the app. and means is supplied for passing current between the electrodes, the space between the electrodes being of const. vol.

Lining metal receptacles electrolytically. J. S. GROFF. U. S. 1,464,506, Aug. 14.

Torpedo flasks or similar metal receptacles are lined by gradual electrodeposition on the flask as a cathode of a thin dense coating of an alloy of Sn and Pb deposited from a Pb fluosilicate soln. within the receptacle to be lined. A solder anode is employed.

Apparatus for the treatment of gases with silent electric discharges. I. SZARVASY. Can. 233,713, Aug. 21, 1923.

Electric furnaces. W. E. MOORE. Can. 233,338, Aug. 7, 1923. A tilting elec. furnace has means for adjusting the electrodes, comprising a motor-driven winch mounted within the transformer housing walls, a cable connected on the electrodes and the winch, means for normally causing the cable to exert a frictional grip on the winch drum and means for automatically releasing the grip when the electrode reaches the upper or lower limit of its movement.

Electric furnaces. J. E. LEONARZ. Can. 233,079, July 31, 1923. The device for cooling the electrodes has a gas inlet port and means for directing currents of gas inwardly along the surface of the electrode.

Mounting for electric furnace resistors. O. A. COLBY and T. A. REID. U. S. 1,464,499, Aug. 14.

Electric hearth resistance furnace. M. SAUVAGEON. U. S. 1,464,543, Aug. 14.

Electric resistance muffle furnace. C. A. CADWELL. U. S. 1,464,496, Aug. 14.

Resistance-wire coils of electric heaters. L. J. FULLER. U. S. 1,464,703, Aug. 14.

Structural features.
Furnace for producing "Misch metal" electrolytically. C. W. BALKE. U. S. 1,464,862, Aug. 14.

Temperature-regulated draw-off plug for electric furnaces. F. POPE. U. S. 1,463,970, Aug. 7.

Alloys. W. B. BALLANTINE. Brit. 192,150, Oct. 25, 1921. Low-C Fe-Cr alloys are made by heating in an elec. furnace a mixt. of chromite or other oxidized Fe-Cr compd. and an alk. earth silicide. The alloy produced may be refined as described in 159,568 (C. A. 15, 2060), and 179,992 (C. A. 16, 3303). One or both of the electrodes of the furnace may be made of Fe-Cr; or, where a carbon electrode is employed, a layer of carbon-free material, such as broken slag, may be interposed between the electrode and the charge.

Glossy galvanic metallic coatings. A. CLASSEN. U. S. 1,464,149, Aug. 7. Glossy metal coatings are produced on metals galvanically, e. g., a Zn coating on Fe, by adding to the electrolyte, e. g., a soln. of ZnSO₄ and (NH₄)₂SO₄, starch degradation products or other colloids and substances easily reducible in the presence of the colloids so as to prevent the generation of H at the cathodes. The galvanizing is conducted in the usual manner except for this alteration. Cf. C. A. 17, 244.

Coating for incandescent lamps. M. LUCKIESH. U. S. 1,464,101, Aug. 7. The exterior of incandescent lamp bulbs is coated with a mixt. of talc, ZnO, Na silicate and H₂O (to which coloring materials may be added) and then with dammar varnish.

Zinc electroplated articles. J. HAAS, JR. Can. 233,149, July 31, 1923. Ferrous articles are coated with a dense bright electrolytic coating of Zn alloyed with Hg.

5—PHOTOGRAPHY

C. E. K. MEES

Note on the theory of photographic sensitivity. S. E. SHEPPARD and E. P. WIGHTMAN. *Science* 58, 89-91(1923).—The theory that the latent image consists of colloidal Ag and that there are also present in the grain, prior to exposure, colloidal Ag specks, which form development centers by exposure are discussed, and exptl. evidence is given that such pre-existent specks do occur and that they are distributed both inside the grain as well as on the surface. It is supposed that the first action of light is to release a photo-electron from the colloid Ag speck, that the free electron, having an av. kinetic energy $1/2mv^2 = h\nu$, where ν is the frequency of the active light, is then able to enter the Ag ion, forming a neutral Ag atom, while the unneutralized Br ion loses an electron. This chain reaction, analogous to that suggested by Bodenstein for the action of light on H₂ + Cl₂, would go on to a limiting state, depending on the initial energy of the photo-electron, but producing a nucleus large enough to initiate development for a developer of given reduction potential.

E. P. WIGHTMAN

Photochemical decomposition of silver bromide. II. ROBERT SCHWARZ and HEINRICH STÖCK. *Z. anorg. allgem. Chem.* 129, 41-54(1923); cf. C. A. 17, 1387.—When AgBr samples of various sizes were exposed to the light from a Hg arc lamp, the amt. of

Br liberated fluctuated extremely and showed by no means a tendency to decrease. Factors influencing these results are (1) the absorbed moisture, whose gradual removal decreased the speed of Br liberation up to the point of complete removal, when the speed rose again; and (2) the grain size, which increased with age. Colloidal sols act catalytically, Pt for example decreasing the speed and SiO_2 increasing it.

G. R. FONDA

High-speed cinematography (CRANZ, BAMES) 24.

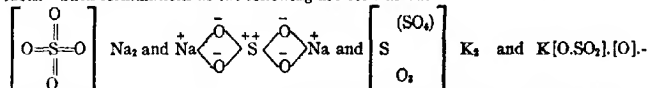
Photographic half-tone screen. M. RUEHLAND. U. S. 1,464,139, Aug. 7. A screen is formed of irregular polygons each of about the same area and positioned so that the boundaries between them have about the same width.

Intaglio printing forms. E. SAUER. U. S. 1,464,140, Aug. 7. A transparent carrier such as celluloid or similar compn. is coated with a layer of dichromated gelatin, an intaglio screen plate is applied to the face of the layer and it is exposed to light through the screen. A dia-positive of the picture is applied to the uncovered side of the carrier and the layer is exposed to light through the dia-positive and then developed with warm H_2O .

6—INORGANIC CHEMISTRY

A. R. MIDDLETON

Old and new theories of coordination. T. M. LOWRY. *Chemistry and Industry* 42, 746-7(1923).—In a review, commendatory in general, of Schwarz-Bass, *Chemistry of Inorg. Complex Compds.*, L. points out the inadequacy of Werner's theory of auxiliary valence and the superiority of modern electronic formulas in portraying the exptl. facts. Such formulations as the following are contrasted:



$[\text{SO}_3\text{O}] \text{K}$, in which the central O atom belongs to both coordination spheres. The coordination theory contributes little or nothing to elucidation of poly-chromates and -silicates but has interpreted clearly for the first time the 42 O atoms characteristic of all phosphomolybdates and allied compds. whether they contain 7, 8 or 9 ionizable H atoms. Water of crystn. and the distinction between ionizable and non-ionizable valencies are discussed briefly.

A. R. M.

Perchromic acid. G. N. RIDLEY. *Chem. News* 127, 81-2(1923).—A review of the formulas, chem. behavior, decomn. and isolation of these compds. No new exptl. material.

A. R. M.

Properties of the metaphosphates of silver. JOHN MISSENDEN AND F. E. LICHTI. *Chem. News* 127, 98(1923).—A review of these salts with reference to the literature.

A. R. M.

Preparation of stibine from alloys. E. J. WEEKS. *Chem. News* 127, 87-8(1923).—From the discrepant results of various workers it is concluded that the same amt. of SbH_3 may be obtained from any alloy of 1 part Sb with 1-4 pts. of Zn.

A. R. M.

Separation of the rare earths by basic precipitation. VI. WILHELM PRANDTL AND JOHANNA RAUCHENBERGER. *Z. anorg. allgem. Chem.* 129, 176-80(1923); cf. *C. A.* 17, 2401.—The nitrates of Ce, La, Pr, Nd and Sm in the presence of equiv. amts. of $\text{Hg}(\text{CN})_2$ in 1-, 2-, 3-, 4- and 5-N NH_4NO_3 soln. at 15°, 30°, 50° and 100° were decompd. with NH_3 . After equil. was attained the amts. of NH_3 and rare earth in soln. were detd. The results obtained were inferior to those previously attained with Zn and Cd. $\text{Ni}(\text{NO}_3)_2$ was similarly investigated. At high NH_4NO_3 concns. and at the higher temps. values obtained with this salt approached those obtained with $\text{Zn}(\text{NO}_3)_2$ but were still inferior to those obtained with $\text{Cd}(\text{NO}_3)_2$. The latter salt which acts most favorably in the sepn. of the rare earths serves best when the equiv. proportions are $3\text{CdO}:1\text{M}_2\text{O}_3$.

L. T. FAIRHALL

The reduction of some rarer metal chlorides by sodium. M. A. HUNTER AND A. JONES. *Trans. Am. Electrochem. Soc.* 44, Preprint(1923).—The success attending the production of metallic Ti from the chloride by the reduction with Na led to exptl. work on the chlorides of Be, Cr, U, V, and Zr. Results were encouraging and reduction of

the pure anhyd. chlorides offers the best means of obtaining the rarer metals in the pure condition. Be, Cr, and Zr were obtained in a more or less granular form while U and V of varying purity were obtained in metallic powders only. Details are given.

W. H. BOYNTON

Chemistry of the platinum metals. IV. Alkali ruthenium double sulfites. II. H. REMY AND C. BRIMMAYER. *Z. anorg. allgem. Chem.* 129, 215-42(1923).—A careful study of the reactions of alkali sulfites on ruthenium chloride. The following new compds. have been prepd.: *potassium trisulfite ruthenate*, $K_4[Ru(SO_3)_2]_3$, of variable water content, dark green needles; *sodium hendecasulfite diruthenate*, $Ru_2(SO_3)_2 \cdot 8Na_2SO_3 \cdot 3H_2O$, yellowish white crystals prepd. by the action of concd. $NaHSO_3$ soln. upon an aq. soln. of sodium pentachlororuthenate; *sodium ruthenoruthenisulfite*, $2Ru(SO_3)_2 \cdot Ru_2(SO_3)_2 \cdot 4Na_2SO_3$ prepd. by the action of a small amt. of $NaHSO_3$ soln. upon a soln. of sodium pentachlororuthenate. This compd. seps. as a dark blue amorphous powder. The study of these various reactions has indicated the existence of other ruthenium sulfite complexes. The exact analysis of the complex ruthenium sulfites and their mixts. was made possible by a newly developed method of sepg. the Ru as tetroxide and detg. the S as $BaSO_4$. In the earlier work of Miolati and Tajiri on the alkali ruthenium sulfites it is apparent that these investigators sepd. no definite compds.

L. T. FAIRHALL

Reduction of thorium, zirconium and titanium dioxides. OTTO RUFF AND HERBERT BRINTZINGER. *Z. anorg. allgem. Chem.* 129, 267-75(1923).—The reduction was effected in a wrought iron bomb of especial construction by means of Na, Ca or Na-Ca alloy. While pure Na reduced the 3 oxides at 900-950° rather indifferently, pure Ca was more effective. A 30% Na-Ca alloy is still better at this temp., yielding 84% Th, 97% Zr and 82.8% Ti. In another expt. the reduction of Th was increased to 96%. The action of the Na-Ca alloy is more evident the more positive the metal acted upon.

L. T. FAIRHALL

Oxidation of complexes of nickel and cyanogen; valence, coordination and color. ANDRÉ JOB AND ANDRÉ SAMUEL. *Compt. rend.* 177, 188-91(1923).—Alkaline reduction of $K_2Ni(CN)_4$ gives a red complex $K_2Ni(CN)_3$; valence 1, coordination number 3; stable in soln. in absence of KCN. If CO is passed into the soln., a colorless complex, coordination number 4, valence 1, is formed. A concd. soln. of $Ni(CN)_2$ in large excess KCN is deep red; spectrophotometric evidence, to be presented later, indicates a new complex of coordination number 6, valence 2, stable only in concd. soln. A violet complex of coordination number 6, valence 3, may be formed by addition of NO to $K_2Ni(CN)_4$, or of KOH and NH_2OH to $K_2Ni(CN)_4$; the provisional formula of the ion is $[Ni(CN)_4(OH)_2(NH_2OH)]^{2-}$.

B. H. CARROLL

The aluminum antimonides (constitutional diagrams for the antimony-aluminum system). G. G. URZOV. *J. Russ. Phys.-Chem. Soc.* 51, 461-71(1919).—Old diagrams by Gauthier and by Campbell and Matthews show 2 max. upon the curve of the beginning crystn. These max. are not well defined, and do not find corroboration in the microstructure, the latter showing one cryst. compd. only surrounded by a eutectic mass lacking uniformity. According to Sade, the compd. AlSb has a low velocity of formation. U. prepd. a stoichiometrically correct alloy by melting the metals, overheating them to about 1150° and keeping there for a time. By melting this compd. with either Sb or Al and taking the cooling curves with the pyrometer of Kurnakov, U. showed upon 18 alloys that only one max. exists; this is at 1062° and at the AlSb compn. the excess of either Al or Sb crystallizing in the eutectical form. Molten Sb dissolves AlSb very easily, while Al dissolves it slowly.

M. G. KORUNSKY

The action of salts on the decomposition of sodium peroxide by water. Y. J. MIUKHLENKO. *J. Russ. Phys.-Chem. Soc.* 53, 350-6(1921).—The reaction $Na_2O_2 + H_2O = 2NaOH + O + 16.01$ Cal. soon stops, but the presence of small amts. of certain salts induces the reaction to proceed to completion to varying extents. 146 different salts, oxides and metals were tested for their catalytic property in this reaction, and the degree of decompn. of the Na_2O_2 was measured by detg. the quantity of O given off in a gasometer at the end of 1, 2 and 5 min., resp. The original should be consulted for the detailed tables of results. The general findings are: The cations alone exercise the catalytic effect whether salts, oxides or pure metal be used. The anions are entirely inactive in this respect. The best catalyzers are the cations of the VIII group, also the cations of Cu, Ag, Au and Mn. These induce the reaction to proceed 50-100% to completion within the first 10 min. The cations of the alk. and alk. earth metals, also of U, Cd, Hg, Al, Sn and NH_4 possess either no or very weak catalytic properties. Finely powd. Al, NH_4SCN , As_2O_3 , $SbCl_3$, and Sb_2S_3 render the reaction explosive. The catalyzers retain their activity in dilns. up to 1 part by weight

to 160 parts of Na_2O_2 . O-rich compds. like KMnO_4 and PbO_2 when used in this reaction are themselves partially decompd. and give off part of their O. Such reaction is expressed as $2\text{KMnO}_4 + \text{Na}_2\text{O}_2 = \text{K}_2\text{MnO}_4 + \text{Na}_2\text{MnO}_4 + \text{O}_2$. Hence the use of compressed sticks of a mixt. of Na_2O_2 with a catalyzer (powd. Cu) in the cartridges of O-yielding masks is recommended.

W. A. PERLZWEIG

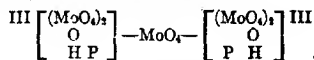
Behavior of calcium oxide in the presence of water. V. KOHLSCHÜTTER AND W. FEITKNECHT. *Helvetica Chim. Acta* 6, 337-69(1923).—CaO was prepd. in various ways from different samples of materials in order to compare their characteristics. When slaked by placing in a bell jar over water, the increase in wt. is linear until one mol. of water is absorbed. The rate then decreases until a limiting value is reached which varies somewhat among the different samples. The lighter or less dense the sample the more rapid is the absorption. The vol. increase during the first portion of the slaking is zero, then almost linear with the absorbed H_2O till one mol. has been absorbed, and then remains the same. The vol. increase like the wt. increase is greater for the less dense powders. A study of the settling times, in H_2O , of these vapor-slaked samples has been made and also the influence of prolonged standing and heating of the ppts. upon these settling times. The influence of the presence of various electrolytes has been investigated. The viscosity of the paste increases with time of standing and varies with the temp. to which it is heated. The ratio of H_2O to CaO in the pressed cake was about 4 to 1. The water is held between the secondary particles which make up the larger discrete grains of the paste. Heating has the effect of compressing or shrinking these particles and increasing the space between them. Paste treated in this way before drying has a higher H_2O content than the normal paste. Microscopic examn. showed the individual particles to be made up of smaller units. The grains became less opaque and more flocculent in character upon heating and standing. Determinations of the heat of hydration of the oxide were carried out in a covered Dewar flask. The av. value obtained was 15,300 cal per mol. The comparative rates of reaction for oxides obtained from different sources were detd. by comparing the temp.-time curves of the calorimeter. The lighter oxides, e. g., those from the burning of oxalate and carbonate slake more rapidly than those from other sources, e. g., from hydroxide. The hydration rate is accelerated by NaCl and CaCl_2 and retarded by NaOH, CaSO_4 , $\text{Ca}(\text{OH})_2$, and NaOAc in the slaking soln. A study was made of the settling rate of the water-slaked ppts. The rate is retarded by standing and by heating. The influence upon the product of the temp. of the water used for slaking is very great but differs decidedly according to the method of prepn of the particular oxide tested; e. g., water of a higher temp. produced a more quickly settling ppt. with CaO from CaCO_3 and a more slowly settling ppt. with CaO from the oxalate.

C. R. PARK

The ternary system: ammonium chloride-ferrous chloride-water. F. W. J. CLENDINEN. *J. Chem. Soc.* 123, 1338-44(1923).—Expts. were conducted at 25° and at 60°. The solids were caught in a Gooch crucible on a fine Ag-gauze plate. Comps. of both solns. and solid in equil. with them for more than 40 expts. are given. The irregularities in the mixed crystals found by Roozeboom (*Z. physik. Chem.* 10, 145) are due to the fact that the FeCl_2 content of the solids varies with the time of shaking up to a period of one day. The compds. $2\text{NH}_4\text{Cl}\cdot\text{FeCl}_2\cdot\text{H}_2\text{O}$ and $\text{NH}_4\text{Cl}\cdot 2\text{FeCl}_2\cdot 4\text{H}_2\text{O}$ were not found; $\text{NH}_4\text{Cl}\cdot\text{FeCl}_2$ and $\text{NH}_4\text{Cl}\cdot 4\text{FeCl}_2\cdot 6\text{H}_2\text{O}$ sepd. out at 60°.

F. E. BROWN

Molybdic acid phosphites and pyrophosphates and the structure of phosphorous acid. ARTHUR ROSENHEIM, MARKUS SCHAPIO AND ALICE ITALIENER. *Z. anorg. allgem. Chem.* 129, 196-205(1923).—The authors have studied molybdic acid phosphite salts of the type $2\text{R}_3\text{O}\cdot\text{P}_2\text{O}_5\cdot 12\text{MoO}_3 + \text{aq}$. The salts of this type are yellowish. The prepn. of the white salts of K, NH_4 and guanidine of the type $2\text{R}_3\text{O}\cdot\text{P}_2\text{O}_5\cdot 5\text{MoO}_3 + \text{aq}$ is also described. On the basis of Miolati's designation of the structure of the molybdc acid phosphates, the phosphites would have the structure



While the Na and Li molybdc acid pyrophosphates could be prepd., attempts to prep. the K and NH_4 salts from solns. of the alkali molybdate and alkali pyrophosphate by the addn. of an acid gave a mixt. of these compds. with the analogous difficultly sol. 12-molybdc acid orthophosphate. Measurements of the phys. consts. of the various salts were made and establish the formula of the yellow molybdc acid pyrophosphate as $\text{R}_4\{(\text{P}-\text{O}-\text{P})(\text{Mo}_2\text{O}_7)_2\}\cdot\text{aq}$. and the yellow molybdc acid phosphite as $\text{R}_4\{(\text{P}-\text{H}-\text{P})(\text{Mo}_2\text{O}_7)_2\}\cdot\text{aq}$. as well as the previously described molybdc acid subphosphate as $\text{R}_4\{(\text{P}-\text{P})(\text{Mo}_2\text{O}_7)_2\}\cdot\text{aq}$. In all 3 series the coordination no. of each

of the phosphorous atoms is 4, while in the heteropolyphosphates the coordination no. is 6.

L. T. FAIRHALL

• **The direct preparation of tetraphosphoric acid.** M. A. RAKUZIN AND A. A. ARSEN'EV. *J. Russ. Phys.-Chem. Soc.* 53, 1, 376-7(1921).—After the addn. of 27.4% by wt. of P_2O_5 to H_2O and after the corresponding amt. of H_3PO_4 had formed, the reaction becomes less violent and the soln. is then capable of dissolving more P_2O_5 up to 520%. This satd. soln. is oily, and after 5 days' standing at room temp. crystals of $H_4P_4O_{13}$ sep. out. This compd. has a m. p. of 34° and d_{15}^{20} 1.8886 (as detd. in toluene of known d). It was also found that MeOH and EtOH will dissolve 295.8% and 258% of P_2O_5 , resp.

W. A. PERLZWRIG

7—ANALYTICAL CHEMISTRY

WILLIAM T. HALL

The treatment of permanganate solutions used for volumetric analysis. G. BRUNNS. *Chem.-Ztg.* 47, 613-5(1923).—Further testimony showing that when pure $KMnO_4$ is dissolved in pure water the soln. keeps indefinitely without change of titer. The reasons for lack of stability of impure solns. are discussed and a plea is made for crystallized oxalic acid as a standard rather than sodium oxalate and the use of pipets for withdrawing the soln.

W. T. HALL

Colorimetric methods with the aid of Wilhelm Ostwald's color norms. F. V. V. HAHN. *Z. angew. Chem.* 36, 366-9(1923).—According to Ostwald every shade of color is made up of 3 parts—a white component, *W*, a black component, *S*, and the full color, *V*. By defining a shade in these 3 ways it is characterized just as the pitch of a tone is by the no. of vibrations. A simple app. is described which enables any one easily to measure these 3 characteristics. The color of any soln. can be measured by matching it against tints on a chart and then repeating with 2 color filters, chosen in accordance with the results of the first comparison. Tables are given showing how the tints obtained with varying concns. of $HMnO_4$, colloidal PbS and ammoniacal Cu can be designated in these terms so that a quantitative analysis can be made for Mn, Pb or Cu by merely measuring the color and referring to the empirical tables. In the long run this should be easier and just as accurate as preparing a set of standards and merely comparing the color of the unknown with that of a known quantity similarly treated.

W. T. HALL

Quantitative separation of arsenic, antimony and tin. G. LUFF. *Chem.-Ztg.* 47, 601-2(1923).—Dissolve the higher sulfides, as obtained by pptn. from alkali sulfide soln., in an aqueous soln. of 5 g. NaOH. Make the soln. neutral, cool in ice water and add HCl until it is 8 *N* in this acid. Ppt. As_2S_3 with H_2S . Dissolve this ppt. in hot dil. NH_3 , oxidize with perhydrol and ppt. Ag_3AsO_3 in neutral soln. Weigh after drying at 120° . Evap. the filtrate from As_2S_3 pptn. to 100 cc. Place the soln. in a buret and det. what vol. is necessary to neutralize NH_3 equivalent to 10 g. NH_4Cl . From this compute the acid in the soln. and dil. so that the soln. will contain in 300 cc. 42 cc. of concd. HCl and 16.7 g. of NH_4Cl (calling the 5 g. NaOH previously added equiv. to 6.7 g.). Under these conditions Sb can be pptd. as sulfide in the presence of Sn. Ignite the ppt. of Sb_2S_3 in CO_2 and weigh. In the filtrate ppt. the Sn as sulfide after neutralization and weigh as SnO_2 .

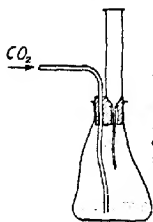
W. T. HALL

New microchemical reactions characteristic for the separation of antimony and tin. A. P. ORTODOCU AND MLE M. RESSY. *Bull. soc. chim.* 33, 991-4(1923).—A soln. of NaCl (not over 18 g. per l.) serves to give characteristic crystals with Sb and Sn in HCl provided not more than 200 g. of $SnCl_2$ or 300 g. of $SbCl_3$ are present per l. As little as 0.06 mg. Sn and 0.08 mg. Sb can be detected and no other element appears to give similar ppts. Place a drop of the HCl soln. on a glass slide and beside it a drop of 1.7% NaCl soln. Carefully make one drop touch the other and evap. to dryness. With Sn 6-pointed star crystals of Na_2SnCl_6 are obtained and with Sb crosses of $NaSbCl_4$. Tests with oxalic acid, tartaric acid, Na pyroantimonate and $HgCl_2$ were found less satisfactory as microchemical tests.

W. T. HALL

Quantitative determination of small amounts of tin and lead. AAGB W. OWE. *Tidsskrift for Kemi og Bergvaesen* 3, 8-15, 31-9(1923).—After having considered the different methods for detn. of small amts. of Sn O. carefully examd. the iodometric ones and concludes by recommending the following procedure: Place the Sn soln. in a 300 cc. Erlenmeyer flask, fitted as shown by the drawing. Dilute with H_2O and HCl to a total vol. of 50 cc. and an acidity of 2.4 *N*. Add 0.4 g. of Al and introduce CO_2 . After a few min. heat the flask gently, but do not boil. Spongy Sn is pptd. When the evolution

of H_2 has finished, boil for about 5 min., shaking occasionally to dissolve Sn. When the Sn is completely dissolved, increase the CO_2 current and cool. After 5-10 min. add 25 cc. of 0.02 N I_2 soln., or more if the amt. of Sn exceeds 20 mg., from a pipet through the funnel, while lifting the stopper. Wash the funnel with a little H_2O , dil. to 200 cc. and titrate with 0.02 N $Na_2S_2O_3$. The following procedure is good for traces of tin.



Ppt. the Sn as sulfide and dissolve in 6 N HCl . Take 20 cc. of this soln. contg. 0.1-3.0 mg. Sn in a 3×18 cm. test-tube, closed by a rubber stopper with two borings and otherwise fitted exactly as the above-mentioned app. Apply a current of CO_2 through the app. and add a thin strip of Zn weighing 0.75 g. When this has dissolved, boil for 2 min. to dissolve the Sn. Then add 2 cc. of a boiling soln. of Schryver's reagent (2 g. of α -dinitrodiphenylamino-sulfoxide in 1 l. 0.1 N aq. $NaOH$) and boil for 5 min. Dil. to 100 cc. with H_2O , filter through an alundum filter-cone and compare in a colorimeter with a standard soln. The concn. of HCl must be exactly equal in both solns. Small amts. of lead can be detd. conveniently by the following procedure: Pb in a faintly aeric soln. contg. about 10 mg. Pb in 50 cc. is pptd. by an excess of $K_2Cr_2O_7$ and the liquid is gently heated for 0.5 hr. on the steam bath to obtain a well formed ppt. Then filter through an Allihn's tube and wash with cold water. Connect the filter tube with a 300 cc. suction flask contg. 70 cc. H_2O , 5 cc. H_2SO_4 , d. 1.29 and 5 cc. 10% KI . Pour 10 cc. 6% HCl through the filter and wash rapidly with cold water, applying a faint suction. Then titrate with $Na_2S_2O_3$ and starch. The error should not exceed 0.1 mg. Pb.

CHR. H. A. SVERTSEN

Report on the determination of iron and aluminium, calcium and magnesium in the ash of seeds. A. J. PATTEN. *J. Assoc. Offic. Agr. Chem.* 6, 418-22(1923).— $FePO_4$ alone is pptd. at p_{H^+} = about 2. $AlPO_4$ is pptd. at p_{H^+} = 3.0-3.5. $Ca_3(PO_4)_2$, however, does not begin to ppt. until the soln. approaches p_{H^+} = 7 and is completed at p_{H^+} = 7.8. When all 3 phosphates are present the Fe and Al phosphates may be sepd. from Ca by adjusting the reaction, with thymol blue as indicator before $NH_4C_2H_3O_2$ is added.

M. S. ANDERSON

Quantitative separation of platinum and iridium. SHIN-ICHI AOYAMA. *J. Chem. Soc. Japan* 44, 427-56(1923).—The principle of the method is based on the following facts. H_2PtCl_6 soln. at acidity less than 0.6 N can be reduced quant. by Cu. $IrCl_4$, on the other hand, will be reduced only slightly (1-3%) at less than N acidity, and the Ir thus reduced if heated in a H atm. is more resistant toward aqua regia than Ir reduced by Mg. The method is to reduce the mixed chloride soln. by Cu in a proper acidity. The metals, contg. Pt and a trace of Ir, are heated in a H atm. and treated with aqua regia which dissolves Pt only. The filtrate is reduced by Cu and Mg in order. By repeating this process twice, Pt free from Ir can be obtained quant. The filtrate from the first Cu reduction, contg. the main portion of Ir, is treated with aqua regia, and then reduced by Mg. After 2 treatments, Ir free from Pt can be obtained. The sum of this Ir and that sepd. from Pt by aqua regia after the first Cu treatment corresponds to the theoretical amt. contained in the mixt. Weighing the metals must be done after roasting them at 550-600° for 30 min. in a H atm. Cu as precipitant is prepd. by dissolving 100 g. of $CuCl_2$ in 1750 cc. of 2.4 N HCl and by gradually adding 35 g. Zn. The Cu is filtered off in an atm. of H and freed from $ZnCl_2$ by the usual HCl treatment. The aqua regia satisfactory for this sepn. should consist of 190 cc. HCl (1.19) + 830 cc. H_2O , and 80 cc. HNO_3 (1.40). Since Pt reduced by Cu contains a small amt. of metallic Cu, it should be redissolved and re-reduced by Mg. Applications of this method to the analyses of metals contg. these 2 elements are given in detail.

S. T.

The separation of the rare earths by basic precipitation. III. The quantitative separation of cerium from the other earths. WILHELM PRANDTL AND JOSEPH LÖSCH. *Z. anorg. allgem. Chem.* 122, 159-66(1922); cf. *C. A.* 14, 2805; 16, 1189, 3599.—A procedure is given, depending on the fact that Ce, unlike the other rare earths, has quadrivalent salts which hydrolyze with sepn. of $Ce(OH)_4$. Compds. of the type $[Co(NO_2)_6(NH_3)_2]$ and $[Co(NO_2)_6(NH_3)_3](NO_3)_2$ oxidize Ce^{III} to Ce^{IV} salts and simultaneously cause pptn. of $Ce(OH)_4$ by neutralizing the acid formed on hydrolysis. By using $[Co(NO_2)_6(NH_3)_2]$, Ce can be detd. quantitatively in Th-free mixts. of the rare earths. The soln. of earth salts is pptd. with $(CO_2H)_2$ in the regular way, the oxalates are ignited, the oxides weighed, dissolved in HNO_3 (with addn. of H_2O_2 at times to reduce the CeO_2), evapd. to dryness, dissolved in 3% NH_4NO_3 , slightly acidified with dil. HNO_3 , $[Co(NO_2)_6(NH_3)_2]$ (4 g. per 1 g. earth oxides) added, and kept at 60° until $Ce(OH)_4$ seps. (the soln. must be kept acid during the 408 hrs. necessary for pptn.). The color, at

first violet-red, becomes dark red, bright red, and brown-red, with the ppt. at first bright yellow, then brownish yellow. The ppt. is filtered, washed with NH_4NO_3 , dissolved in warm dil. HNO_3 + H_2O_2 , evapd. to remove H_2O_2 , dild. with H_2O , pptd. at 100° with $(\text{Co}_2\text{H})_2$, and the $\text{Ce}_2(\text{C}_2\text{O}_4)_3$ incinerated. The purity of the Ce_2O_3 obtained is tested by dissolving in concd. HNO_3 and H_2O_2 , concg. and examg. spectroscopically for other adsorbed earths. To det. the other earths in the $\text{Ce}(\text{OH})_3$ filtrate, the latter is treated with concd. HNO_3 , boiled until clear, excess NH_4OH and H_2S are added; it is let stand, decanted, the residue washed with dil. NH_4OH , digested with NH_4S , washed and treated with HNO_3 . The earths dissolve by filtering, are freed from CoS and S and are pptd. in acid soln. by $(\text{Co}_2\text{H})_2$. Typical analyses are given. C. C. DAVIS

Contribution to the microscopic detection of iron. OSWALD RICHTER. *Z. Mikroskopie* 39, 1-28(1922); *Physik. Ber.* 3, 1149(1922).—To detect Fe inside the plant cells, cuttings made with a brass knife were boiled $1/2$ min. in concd. NH_3 , washed, and treated with 2% K_4FeCN_6 soln., again twice washed and treated with 10% HCl . A series of results is given and discussed which are of botanical interest exclusively.

A. E. STERN
The titration of very small amounts of gold. W. B. POLLARD. *Bull. Inst. Mining Met. Eng.* 1923, No. 225, 7-8; cf. *C. A.* 17, 2033.—In dissolving 0.5 g. of Au the best results were obtained with 2 cc. of concd. HNO_3 and 6 cc. of concd. HCl . The rate of dissolving was slower if either of the acids was added in excess. W. T. H.

Sensitiveness of qualitative reactions. IV. The chromium ion and the chromate ion. O. LUTZ AND J. JACOBY. *Latvijas Augstskolas Raksti* 3, 109-37(1922).—In the detection of Cr, it is advisable to convert trivalent Cr into hexavalent Cr, the reactions of the CrO_4 anion being generally more sensitive than those of the Cr cation. Fusion with KNO_3 or KClO_4 is preferable to fusion with Na_2O_2 or K-Na carbonate and KNO_3 for this purpose, while treatment with Na_2O_2 , with NaOH and H_2O_2 , or with NaOH and Br may also be employed. The sensitiveness of different tests, expressed in g. of Cr per 5 cc. of soln., is as follows: pptn. of Cr cation by NH_4OH or NaOH in the presence of NH_4 salts, 15×10^{-2} ; pptn. of Cr cation by NaHCO_3 and NH_4Cl , 17×10^{-2} ; pptn. of CrO_4 anion by AgNO_3 , or, in the presence of NH_4 salts and acids, by $\text{Hg}(\text{NO}_3)_2$ and HNO_3 , 52×10^{-2} ; colorimetric estn. of CrO_4 anion by reaction with H_2O_2 in the presence of H_2SO_4 , 26×10^{-2} . The borax bead and Na metaphosphate bead tests are recommended for orientation. J. S. C. I.

The determination of sulfur in cast iron. SANSEI KITAJIMA. *Bull. Inst. Phys. Chem. Res. (Japan)* 2, 243-58(1923).—An excellent summary of the precautions necessary to obtain good results by the evolution method. K. KASHIMA

Nitrogen in steel. C. B. SAWYER. *Trans. Am. Inst. Mining Met. Eng.* 1923, No. 1252S, 31 pp.—The distn. method of Hurum and Fay (*C. A.* 16, 883) was modified slightly. Preliminary tests showed that (1) pieces of Zn placed in the distg. flask prevented bumping; (2) an ordinary Erlenmeyer flask, loosely stoppered, could be used as receiver; (3) a slightly modified Kjeldahl trap and a piece of glass wool inserted between the distg. flask and condenser prevented mechanical spurring over of traces of NaOH ; and (4) a fused quartz condenser tube prevents contamination of alkali but with an ordinary glass tube, alkali equiv. to 0.03 mg. N is obtained. The sample of steel was dissolved in a small glass flask which was connected with a condenser and with a trap contg. freshly distd. HCl . The distg. app. had ground-glass connections or Hg seal wherever there was a junction before the condenser. Before introduction of the FeCl_3 soln., 400 cc. of distd. water and 50 cc. of NaOH soln. were boiled until 1 cc. of 0.01 N H_2SO_4 added to 25 cc. of distillate was recovered by iodide-iodate titration with $\text{Na}_2\text{S}_2\text{O}_8$. In all samples examd., results by the distn. method agreed closely with those obtained by direct combustion of the steel in carefully purified O_2 . Cuts of the complete app. for both methods of analysis are shown and should be consulted by any one attempting to reproduce the results. The results of many analyses show that when Fe is melted under an atm. of N_2 , the following formula holds for the N absorbed: $\% \text{N} = 0.2 \sqrt{P_N}$, where P_N is the pressure in atm. during the melting and solidification. Microscopic examn. of ingots melted under N_2 reveals no trace of N up to approx. 0.03% and indicates the formation of a solid soln. of N in Fe. Above 0.03%, needles of N are found. Fe catalyzes the dissociation of NH_3 at high temps. and is denitrified by H_2 so that it is difficult to effect uniform nitrification by heating in NH_3 . Uniformly nitrified, thin steel disks contg. up to 1.7% N can be produced by heating the unevenly nitrified material with 3-4% N. The decomn. thus produced was shown by plotting $\% \text{N}$ vs. temp. and the general shape of the curve resembles that of volatile solutes in non-volatile solvents. Transformation points obtained with these disks indicate the existence of an Fe-N equil. very similar to the Fe-C one. The eutectoid point is at 1.7% N at 620° .

on heating. Results of bending tests show a marked loss in ductility when the N content exceeds 0.03%. In unevenly nitrified disks, a second eutectoid is indicated microscopically and by thermal analysis with a little over 3% N and at about 693° on heating.

W. T. HALL

Microchemical detection of nitrogen in mineral and organic substances. A. J. NESCU AND C. HARSOVESCU. *Bull. soc. chim. România* 4, 61-5(1923).—N combined as NH_3 in inorg. substances, or in such a form in org. materials that it is liberated as NH_3 on heating the substance with soda-lime, can be detected microchemically by directing the evolved gases on to the surface of a drop of picromalonic acid reagent (satd. soln. of picric acid in Et malonate), or a satd. soln. of picric acid in EtOH contg. 5% of glycerol. Characteristic yellow crystals of NH_4 picrate are produced, *vis.*, more or less elongated prisms with the alc. reagent, which is the more sensitive, and small quadratic crystals with the picromalonic reagent. The reaction is sensitive to amts. of NH_3 as small as 0.1 mg., and it is sp. for this substance, as compared with the volatile amines.

J. S. C. I.

Report on nitrogen. I. K. PHELPS. *J. Assoc. Offic. Agr. Chem.* 6, 391-8(1923); cf. *C. A.* 16, 3450.—A collaborative study was made of the Devarda alloy method and the H. C. Moore method for detn. of nitrates. Tables of the collaborative results are given. It is recommended that a study be made of the Devarda method as applied to nitrates of commerce and that the Moore method be further studied by collaborators. It is furthermore recommended that the use of $\text{Na}_2\text{S}_2\text{O}_8$ as a substitute for Na_2S or K_2S be investigated.

M. S. ANDERSON

Estimation of ammonia without resorting to distillation. SANDER. *Union pharm.* Nov. 1922; *Répert. pharm.* 35, 167-8(1923); cf. *C. A.* 16, 1057.—About 17 g. of the NH_4 salt is placed in a calibrated flask and sufficient H_2O added to make 250 cc. Of this soln. 25 cc. are introduced into a conical flask. In another flask pour 5 to 10 cc. of 40% HCHO soln. and add 20 cc. of H_2O . If the HCHO soln. is acid it should be neutralized with 0.1 N NaOH, phenolphthalein being used as indicator. Pour the HCHO soln. into the ammoniacal soln., shake and titrate with 0.1 N NaOH just to a red color. The no. of cc. of NaOH shows directly the NH_3 content.

A. G. DUMÉZ

Simplified method of estimating ammonia. M. BALLEGH. *Z. Leder- u. Gerberei Chem.* 2, 27-30(1922).—The NH_4 salt soln. is distd. with NaHCO_3 , and the NH_3 collected in 0.1 N acid or 3% boric acid soln. The whole of the NH_3 has passed over when more than $\frac{1}{3}$ of the liquid in the distg. flask has been evapd.

J. S. C. I.

Detection of fluorine in pyrites, blends, calamines, carbonates, silicates, etc. BIEBLAIRE THROPHILE. *Bull. Fédération industr. Chim. Belg.* 1922, 281-4, 327-8; *Chem. Zentr.* 1922, IV, 212, 783.—No new reactions for F are given but directions for the rapid quant. detn. making use of the etching action of HF and the decompn. of SiF_4 with water, NH_3 , 5% NaCl and NaOH. Since F occurs as CaF_2 in F minerals the quant. estn. of F is best accomplished by detg. the total CaO and the CaO in combination other than with F.

C. C. DAVIS

Determination of iodide and iodate. SVEN HASSELSKOG. *Stensk Farm. Tids.* 27, 269-75(1923).—A soln. of KI free from I was prepd. and the iodide detd. by Volhard's grav. method, the Müller and Wegelin method (*C. A.* 8, 1072), and a modification of the latter. The modified method is as follows: To 10 cc. of the soln. contg. iodide add 1 cc. dil. H_3PO_4 , about 50 cc. H_2O and an excess of HIO_3 soln. After 3 min. add enough of satd. Na_3PO_4 soln. to make the mixt. alk. to litmus. An excess does not matter. Then add 1 g. NaHCO_3 (free from CO_3^{--}) and sufficient KI to hold all the I in soln. Titrate with 0.1 N As_2O_3 . 1 cc. = 0.01058 g. I. The results from all 3 methods were identical. The advantage in the modification is the avoidance of CaH_2 extn. and a very appreciable saving of time. The reverse of the reaction admits of detg. MIO_3 . In these tests 0.1 N KIO_3 soln. was matched against the 0.1 N As_2O_3 with the result that 25 cc. took 24.85 cc. of the latter and 1 cc., 0.98 cc. (micro-buret). A series of intermediate amounts from 1 to 25 cc. was equally satisfactory.

A. R. ROSE

Distribution of iodine between chloroform and starch solution with and without the addition of potassium iodide. J. B. FIRTH AND F. S. WATSON. *J. Soc. Chem. Ind.* 42, 308-10T(1923).—In titrating a soln. contg. starch and in contact with CHCl_3 the latter is colored before the former unless considerable KI and starch are present. If the aq. soln. contains 4 g. of starch and 0.384 g. of KI per liter the addn. of I_2 colors the starch before enough is added to color the CHCl_3 . In the absence of KI, the blue color of starch can be dissipated by shaking with CHCl_3 . In other words, KI favors the formation of iodide of starch and owing to the formation of KI, prevents the dissolving of I_2 in non-aq. solvents.

W. T. HALL

The volumetric determination of phosphorus. W. A. TURNER. *J. Assoc. Offic.*

Agr. Chem. 6, 409(1923).—Expts. conducted to test the reliability of the Pemberton volumetric method for P showed that this method gave results uniformly about 8% higher than those obtained by the gravimetric method. It is thought that the ppt. consists of an acid ammonium phosphomolybdate $(\text{NH}_4)_3\text{HPO}_4 \cdot 12\text{MoO}_3$ or $\text{NH}_4\text{H}_2\text{PO}_4 \cdot 12\text{MoO}_3$ together with a certain amount of occluded molybdic acid. The error is const. and when a factor is applied results are satisfactory.

M. S. ANDERSON

The sensitiveness of the reaction between sulfites and silver nitrate. O. HACKL. *Chem.-Ztg.* 47, 466(1923); cf. *C. A.* 17, 1930.—Five cc. and 10 cc. portions of a soln. contg. 0.1 mg. SO_3^{--} per cc. added to 100 cc. H_2O gave no trace of a reaction with AgNO_3 , even upon long standing. 3, 5 and 9 cc. of H_2O mixed with 1 cc. of the same SO_3^{--} soln. gave ppts. or cloudiness with AgNO_3 , but $9\frac{1}{2}$ cc. H_2O and $\frac{1}{2}$ cc. SO_3^{--} failed to react with AgNO_3 . One can detect therefore 0.1 mg. SO_3^{--} in 10 cc. soln. It was noteworthy that the reactions take place with greater ease the smaller the quantities of solns. of the same concns. that are used, a fact dependent upon the quantities of solvent present, and not due to oxidation.

W. C. CRAUGH

The determination of persulfo acids. R. WOLFFENSTEIN AND V. MAKOW. *Ber.* 56B, 1768-71(1923).—In the electrolytic production of persulfuric acid, solns. are obtained which contain H_2O_2 , H_2SO_4 and $\text{H}_2\text{S}_2\text{O}_8$. In the analysis of such solns. it is customary to det. the total active O by adding an excess of standard FeSO_4 soln., heating and detg. the excess with KMnO_4 , then that corresponding to the H_2O_2 and H_2SO_4 and the $\text{H}_2\text{S}_2\text{O}_8$ by difference. The H_2O_2 present can be detd. by direct titration with KMnO_4 . Recently Palme (*C. A.* 15, 1469) has claimed that the detn. of H_2O_2 in this way is influenced by the H_2SO_4 , which under certain conditions can react with H_2O_2 to form H_2SO_4 , H_2O and O_2 . Expts. show that such side reactions may indeed take place but by sufficient diln., low temps., addition of MnSO_4 soln., and rapid titration, the error can be largely avoided. An attempt was made to det. H_2SO_4 directly by treatment with KI and titration with $\text{Na}_2\text{S}_2\text{O}_3$. The $\text{H}_2\text{S}_2\text{O}_8$ reacts very slowly with KI but H_2SO_4 reacts instantly. By keeping the temp. low and diluting considerably it was found possible to get fairly good results but the color often returned after the titration was completed. This was found to be caused by gradual conversion of the $\text{H}_2\text{S}_2\text{O}_8$ into H_2SO_4 . This transformation can be prevented by reducing the acidity of the soln. with AcONa and it was found advisable to substitute Na_2SO_3 soln. for KI and $\text{Na}_2\text{S}_2\text{O}_3$. To det. H_2O_2 , H_2SO_4 and $\text{H}_2\text{S}_2\text{O}_8$ in the presence of one another (1) titrate the H_2O_2 directly with KMnO_4 ; (2) add a large excess of AcONa and titrate the H_2SO_4 with $\text{Na}_2\text{S}_2\text{O}_3$ soln. contg. 2% alc., using a drop of I soln. as indicator; and (3) det. $\text{H}_2\text{S}_2\text{O}_8$ by heating with an excess of FeSO_4 soln. and titrating the excess with KMnO_4 .

W. T. HALL

The detection of sulfate in ferric iron solutions. F. L. HAHN. *Ber.* 56B, 1733(1923).—If 0.4–0.8 g. of Fe_2O_3 is dissolved in acid and tested for SO_4 , the test will be negative if no more than about 0.1% of SO_4 is present but if hydrazine hydrate is added and the soln. is heated, as little as 0.02% SO_4 can be detected with BaCl_2 . Hydroxylamine hydrochloride and ammonia can also be used for the reduction.

W. T. H.

New reactions for the detection of hydrocyanic acid. JEAN PÉSET AND JAVIER AGUILAR. *Arch. méd. legal* (Portugese) 1, 18–21(1922).—The reaction of Pagenstecher and Schönbein for the detection of HCN is studied. It is carried out by dipping a piece of filter paper into a soln. of tincture of guaiac, drying the paper, moistening it with CuSO_4 and suspending it in a bottle contg. the suspected material; if HCN is present the paper turns blue. The CuSO_4 cannot be replaced by salts of Mn, Zn, Co, Ni, Mg, Ca, Sb, Li, Ni, U, Cr, Ta, Ti, Hg⁺⁺, Fe⁺⁺⁺, Sn⁺⁺, or Sn⁺⁺⁺⁺ but the tincture of guaiac can be replaced by other color-forming substances such as an alkaline solution of fluorescein which gives a beautiful green, pyrimidine which gives an intense violet, benzidine an intense blue, aloin a red color, dimethylparaphenyldiamine a Burgundy-red, para-diaminodiphenylamine a rapidly disappearing light bluish green, tetramethylparaphenyldiamine a violet color.

MALCOLM H. SOULE

The estimation of glycerol. S. FACHINI. *Chem. Trade J.* 73, 127–8(1923).—A critical examn. of the KMnO_4 method as developed by Benedikt and Zsigmondy, the $\text{K}_2\text{Cr}_2\text{O}_7$ method proposed by Legler, Burkhardt, Cross-Bevan-Helmer and by Plauen-Herbig-Suhr, the nitroglycerin method of Champion, Pellet and Levkovitsch, the triacetin method of Benedikt and Cantor, the isopropyl iodide method of Zeisel and Panto, the acrolenin method of Ztzsche, direct weighing after acetone extrn. as proposed by Shukoff and Schestakoff, Fachini and Dorta and several other methods, indicated that the $\text{K}_2\text{Cr}_2\text{O}_7$ and acetin methods were on the whole the most reliable. In theory, the latter seems the sounder in principle but it is so sensitive that it is likely to lead to error. A modification is suggested in which the glycerol content is based not upon the dichromate consumption but upon the quantity of CO_2 evolved. Glycerol reacts with 14 equiva-

lents of $K_2Cr_2O_7$ to form 3 mols of CO_2 but 1 mol. of trimethylene glycol unites with 16 equivalents of $K_2Cr_2O_7$ to form 3 mols. of CO_2 . The procedure is as follows: Tare a thin glass flask of 50 cc. capacity. Add 20 g. H_2O and 4-5 drops of the glycerol to be analyzed. Also introduce 1.5 g. of $K_2Cr_2O_7$, weighed accurately. Stopper the flask with a 3-hole rubber stopper carrying a small tap funnel, a tube for the entrance of air reaching nearly to the bottom of the flask, and a tube for the exit of the gas. The exit tube is connected with a 2-bulb tube and a water condenser to condense as much as possible of the steam. After the condenser the gas is passed through H_2SO_4 and $CaCl_2$ and the CO_2 absorbed as in a combustion. After the flask has been properly connected stop the entry of air and add 9 cc. of concd. H_2SO_4 dropwise through the tap funnel. After the evolution of gas slackens, heat the contents of the flask for 2 hrs. by immersion in a beaker of boiling water. Continue the heating 45 min. longer with a current of air passing. Then detach the absorption bulb and transfer the contents of the flask to a 500-cc. measuring flask and make up to the mark at 20° . In a 50-cc. aliquot det. the excess of $K_2Cr_2O_7$ iodometrically. Compute the analysis from the following data: 1 g. $CO_2 = 0.5752$ g. glycerol or 0.6975 g. glycerol, 1 g. of glycerol = 7.456 g. $K_2Cr_2O_7$ and 1 g. $K_2Cr_2O_7 = 0.7748$ g. glycerol. If $B =$ wt. of reduced $K_2Cr_2O_7$, $B_1 =$ theoretical quantity of $K_2Cr_2O_7$ reduced as detd. by CO_2 formed, and $G =$ approximate quantity of glycerol calcd. from CO_2 , then $(B - B_1)/0.7748 =$ wt. of trimethylene glycol and $G - (92.06 \times \text{wt. glycerol})/76.6 =$ wt. of glycerol. W. T. HALL

Comparative experiments with different methods for determining maltose formed by hydrolysis of starch. K. JOSEPHSON. *Ber.* 56B, 1758-61 (1923).—The detn. of maltose formed by the hydrolysis of starch is usually based upon the reducing power of maltose as shown toward an alk. Cu soln. The most convenient way of carrying out the analysis is that recommended by Sonntag (*Arb. Kais. Ges.-A.* 19, 447-57; *Chem. Zentr.* 1903, I, 998) and by Bertrand (*Ber.* 51, 780) but Willstätter, Waldschmidt-Leitz and Hesse (*C. A.* 17, 2802) have recently claimed that the hypiodite method of Willstätter and Schudel is more reliable. The results published in this paper, however, indicate that the former method is just as reliable. W. T. HALL

The microdetermination of methyl and ethyl groups in the presence of each other. W. KÜSTER AND WILHELM MAAG. *Z. physiol. Chem.* 127, 190-5 (1923).—Willstätter's method (*C. A.* 5, 3452) is modified so that instead of weighing the Me_2NI and $MeEtNI$ directly, the I is weighed as AgI . The app. described by Pregl is so modified as to insure the complete absorption of the alkyl iodides. Imido alkyl groups may be detd. along with alkoxy alkyl groups by conducting the heating for the former at $220-300^\circ$. The combination of Pregl's and Willstätter's app. for the purpose is described. R. L. S.

Detection of pyridine. A. GORIS AND H. LARSONNEAU. *Bull. soc. chim.* 33, 994 (1923).—References are cited to show priority of the work of G. and L. on the detection (cf. *C. A.* 16, 886) over that of Lehner (cf. *C. A.* 17, 252). R. L. BROWN

Quantitative determination of methanol, particularly in sulfite alcohol. SVERRRE LAUNY. *Tidsskrift for Kemi og Bergvaesen* 2, 11-5, 32-6 (1922).—A comparative study of the methods of Reif, Bauer, Paziienti, Denige, v. Fellenberg, Schmiedel, Thorp and Holmes and Koenig indicated that Koenig's method (*C. A.* 7, 860) is the most reliable and Denigés (*C. A.* 4, 1725) only slightly less so. The weak points of all the other methods are discussed in detail. C. H. A. SYVERTSEN

The detection and the quantitative determination of chlorine compounds in benzaldehyde. F. UTZ. *Deut. Parfumerieztg.* 8, 71-4, 96-8; *Chem. Zentr.* 1922, IV, 408.—A description of several methods, especially the latest improved combustion method of Schimmel & Co. (cf. *C. A.* 16, 3046). The method of Baubigny and Chavanne (*Compt. rend.* 136, 1197; 138, 85) was simplified by a change in the app. by using a simple spherical flask for the decompn. and a spherical receiver for collecting the Cl in the sulfite soln. Testing of the method with $PhCHO$ to which were added increasing amts. of $PhCl$ gave satisfactory results. C. C. DAVIS

8—MINERALOGICAL AND GEOLOGICAL CHEMISTRY

EDGAR T. WHERRY AND EDW. F. HOLDEN

What can radioactive methods accomplish in the determination of the age of minerals? G. KIRSCH. *Naturwissenschaften* 11, 372-80 (1923).—A detailed discussion of recent results in the estn. of the age of minerals by radioactive methods, with representative calcs. C. C. DAVIS

Linnæite from Littfeld, Westphalia, and copper blende containing zinc from Sinaloa, Mexico. A. EICHLER, M. HENGLEIN AND W. MEIGEN. *Centr. Mineral. Geol.*

1922, 225-7; *Chem. Zentr.* 1922, III, 704.—Linnacite from the Viktoria mine at Littfeld is composed of crystals with a max. size of 1 cm. including octahedrons with (100), (432) and (113) and d. 4.85. These crystals were accompanied by chalcopyrite, Pb blende and millerite. Analysis indicated the formula $(\text{Co}, \text{Ni})_2\text{S}_3$ in which the ratio Co:Ni is 5:6, with 1% replaced by Fe. This analysis is probably closer to the true compn. than former ones, which were doubtful because of admixtures. The Mexican Cu blende occurred in a Au vein, with free Au and tile ore, as a steel-gray soft ore. Analysis: Cu 51.75, Zn 11.72, Fe 7.73, Pb 0.55, Au 1.90, S 23.14, Te 0.91, gang 2.83%; part of the Cu is thus replaced by Zn and Fe. C. C. DAVIS

A new formation (?) of fluorite. H. HIRSCH. *Z. Krist.* 57, 94; *Chem. Zentr.* 1922, III, 704.—If silicate rocks are not decompd. in the ordinary way with HF + H_2SO_4 , but are treated with HF alone (on account of radioactive measurements) there remains an insol. residue consisting partly of fluorite. This is composed of coarse grains (mostly twinned cubes with a max. side of 0.2 mm.) or fine crystals (not over 0.03 mm. on a side) consisting mostly of many-sided crystals which are not twinned, according to the time and method of decompn. C. C. DAVIS

The mineral danubite. B. MAURITZ. *Centr. Mineral. Geol.* 1923, 178-9; *Chem. Zentr.* 1922, III, 709.—Though Krenner in 1910 described a rock consisting of nephelite, amphibole, hypersthene and traces of a Ca-Na-feldspar named "danubite." M. could find no such primary rock. Examin. of the original transparent section proved that nephelite does not occur in it, but instead labradorite in the form of 6-sided platelets. The material is then a typical amphibole-hypersthene-andesite. The term "danubite" should be abandoned. C. C. DAVIS

The problem of the combination of water in zeolites. O. WRIGHT. *Centr. Min. Geol.* 1922, 164-78, 201-8; *Chem. Zentr.* 1922, III, 702-3.—The close agreement of the exptl. results of W. (cf. *Sitzungsber. Ges. Beförderung gesamten Naturwiss. Marburg* 1919, No. 5; *Chem. Zentr.* 1920, 242) I, with those of Scheumann (cf. *C. A.* 15, 3804) is emphasized, but it is not considered that the break in the dehydration curve at the 0.5 mol. value for the heulandite reported by Scheumann is exptly. verified. Both investigations show that heulandite contains no H_2O combined such as that in ordinary hydrated salts, but at the best as a special kind of solid soln. which as a result of the directing forces of the relatively rigid silicate lattice on the easily mobile H_2O component shows an analogy to true hydrates. Contrary to Beutell (cf. *C. A.* 17, 515) it is maintained that (1) the practically complete reversibility of hydration and dehydration at temps. below 180° are proved exptly. and also that Scheumann has shown that (1) no permanent change is caused by dehydration up to a H_2O content of 3 mols.; (2) contrary to Beutell the curve at low temps. shows almost complete continuity; (3) the breaks in the curve would not appear at higher temps. with integral mols. if any considerable decompn. actually occurred; (4) the curves of Scheumann and W. conform to one another closely up to 200° though the preliminary treatment of the material was different in each case; (5) no evidence was found by optical expts. of decompn.; and (6) Stoklossa observed by optical means no decompn. of the mol. when dehydrated to 2.5% H_2O . Beutell has not proved his assertion that zeolites contain H_2O combined in a manner similar to hydrated salts. C. C. DAVIS

The occurrence of francolite in stony meteorites. H. C. DAS-GUPTA. *Proc. 7th Indian Sci. Cong.* 1921, cxl.—Considered chemically the meteoritic constituent supposed to be identical with the mineral francolite appears to be more closely allied to apatite than to francolite, though the phys. characteristics do not give any conclusive answer. The condition of consolidation indicates that there must be some important difference between this mineral and apatite. C. C. DAVIS

Origin and formation of the ores of middle German copper shale. R. LANG. *Z. deut. geol. Ges.* 73B, 204-23(1921); *Chem. Zentr.* 1922, III, 706-7.—The origin and character of the deposits of the ores of middle German Cu shale are explained. The theories of syngenetic and epigenetic origin are discussed and arguments are given against epigenesis. C. C. DAVIS

The Hohenburg magnesite deposit between Troifach and Oberdorf an der Lamming. E. KRRRL. *Verh. geol. Staatsanst. Wien* 1920, 91-111; *Chem. Zentr.* 1922, III, 708.—In the secondary limestone, phyllite, quartzite and dolomite residues (partly of the same age as magnesite) there is an irregular mass formation of magnesite. Three superficially different types of dolomite and cryst. granular magnesite were studied and analyzed, with analyses of white soft talc (cf. *Verh. geol. Staatsanst. Wien* 1919, 160; *Neues Jahrb. Mineral. Geol.* 1922, I, 173) and greenish shale. The data are compared with the neighboring Wiesergut deposit which is similar in formation. Genetically the deposits do not give evidence of being metasomatic. Contrary to Redlich and Leitmeier

dolomite is not considered as the product out of which $MgCO_3$ is formed; both were originally formed together according to the concn. of the reacting substances. The greater part of the talc, similar to the magnesite, is of hydrothermal formation.

C. C. DAVIS

Phosphate in the Permian Red Beds of Oklahoma and Texas. A. C. SHRAD. *Chem. Age* (N. Y.) 31, 319-20(1923).—Analyses are given, with a theory of the formation of the deposit.

E. H.

The presence of charcoal in carbonaceous mineral coal of the Ostrau-Karwiner region. W. PETRASCHIECK. *Verh. geol. Reichsanst. Wien* 1921, 149-50; *Chem. Zentr.* 1922, III, 710. —Charcoal occurs in thin beds on seams of coal and is composed of small scales with a max. thickness of 1 cm. and an av. diam. of 2 cm. The charcoal is poor in volatile components and it gives a powdery coke. Inclusions of charcoal do not occur in the fat coals of the Ostrau-Karwiner district but do occur in the seams of the upper Ostrau beds and still more often in the Karwiner seams. These inclusions are detrimental to the quality of the coke obtained. The consecutive layers of charcoal in one locality and the complete absence in another indicate that the charcoal was not formed as a result of forest fires.

C. C. DAVIS

An interesting veined rock in the Euganei hills. L. MADDELENA. *Atti Ist. Veneto* 81 (11), 245-51(1921-2).—A detailed description, with many data, of an outcrop of granular rock comprising syenite with veins of gabbro (cf. *Neues Jahrb. Mineral. Geol.* 1884, II, 1893, 1). The syenite is porphyritic and is surrounded by whitish trachytic rock, in which is a vein of basalt notable for the large amt. of hornblende. Microscopic examn. shows basaltic hornblende, Na-Ca feldspar in equal proportions, magnetite, a small amt. of monoclinic pyroxene but no olivine or biotite. The groundmass is composed of feldspathic microlites, hornblende and magnetite. Petrographic study and chem. analysis indicate that the occurrence represents an amphibolitic-diopside andesite, an apophysis of an andesite mass at a greater depth. Further data are given on the individual constituents.

C. C. DAVIS

Occurrence of garnetiferous sillimanite gneisses, scapolite gneisses, and the associated marble beds in the Coimbatore district. L. A. NARAYANA IYER. *Proc. 7th Indian Sci. Cong.* 1921, cxl.—Garnet sillimanite rocks and scapolite gneisses (associated with marble beds) occur in the southern portion of the Coimbatore-taluk near Madukkarai and on the hills west to Waliyar. From the abundance of sillimanite, quartz and graphite in the garnet rocks it is concluded that the latter are metamorphosed sedimentaries. The scapolite gneisses and marble beds probably originated similarly to the Khondalite series of Walker.

C. C. DAVIS

Deposit of bitumen in a lava-cavern in Bombay. D. N. WADIA. *Proc. 7th Indian Sci. Cong.* 1921, cxxxv. cxl.—A cavity (25 ft. long) occurs in thick sheets of basalt contg. coralloidal stalactitic and arborescent masses of prehnite covered by thick layers of asphalt, brilliant transparent crystals of trigonal quartz with pyramidal terminations, powdery zeolites and stilbite. It is suggested that the cavern is a lava geode and the bitumen has accumulated by processes analogous to the excretion of zeolites: Alk. waters have dissolved the small amt. of diffused bituminous material from the tuffs and ashes in the vicinity and collected it in the cave. Such bitumen occurs in the inter-trappcan ash beds of Worlee.

C. C. DAVIS

Gases occurring in nature. IV. F. HENRICH AND G. PRELL. *Ber.* 56B, 1259-62(1923); cf. *C. A.* 17, 1204.—Analyses are given of gases from a number of springs.

D. MACRAE

Movements of the earth's surface crust (JULY) 3. Geology and ground water of the Sacramento Valley, Cal. (BRYAN) 14.

9—METALLURGY AND METALLOGRAPHY

D. J. DEMOREST, ROBERT S. WILLIAMS

Notes on recent progress and the present status of the metallurgy of zinc, aluminium and nickel. MARCEL FOURMENT. *Rev. metal.* 20, 469-80(1923).—A review.

A. PAPINEAU-COUTURE

Lead in 1922. C. E. SIEBENTHAL AND A. STOLL. U. S. Geol. Survey, *Mineral Resources of U. S., 1922*, Pt. I, 27-36(preprint No. 4, publ. July 17, 1923). E. J. C.

Zinc in 1922. C. E. SIEBENTHAL AND A. STOLL. U. S. Geol. Survey, *Mineral Resources of U. S., 1922*, Pt. I, 37-52(preprint No. 5, publ. July 18, 1923). E. J. C.

Tests of low-grade and complex ores in Colorado. WILL H. COGHILL AND C. O.

ANDERSON. *Bur. of Mines, Tech. Paper 283* (1923).—The primary sulfide ores in Colorado are in many instances of too low grade to be profitably exploited. Mining men of the state are much concerned and the investigation described was the 1st step toward reviving the industry. Field investigations of the low-grade and complex ores were conducted to det. approx. quantities of such ores. In such cases as quantity warranted exptl. treatments were conducted in the lab. Eleven oxidized ores were tested, most of the work consisting of cyaniding; a few flotation tests were made. The results were encouraging and justify plans for elaborate tests where available tonnage is adequate.

H. C. PARISH

Solubility of gold amalgam in cyanide solutions. H. A. WHITE. *J. Chem. Met. Mining Soc. S. Africa* 23, 170-1, 218-9 (1923).—In the direct recovery of Au lower residues were obtained when the use of Hg was eliminated. Expts. were carried out in solns. (0.027% KCN, 0.02% NaOH satd. with O₂) with pure Au and as thinly amalgamated Au as possible. It clearly showed that Hg reduced the rate of soln. of Au to nearly 1/2 its original rate. Per 24 hrs., pure Au lost 9.5 mg., while the amalgam lost 5.1 mg. The ratio of these two values is 1.8. This ratio also confirms the deduction that metals sol. in cyanide solns. have their relative rates of soln. proportional to their chem. equiv. Thus 2 Au/Hg is 1.9. This indicates that a Hg film of the thickness employed is attacked in much the same way as pure Hg while the limit to the rate of soln. of the Au is the speed with which it can diffuse through the thin layer of Hg. E. F. P.

Fundamentals of amalgamation. A. W. ALLEN. *Eng. Mining J.-Sci.* 116, 275-80 (1923).—A review of practical aspects. E. J. C.

Use of hot, dry, moist and oxygenated blasts in gas producers, cupolas, and blast furnaces. J. SIGLÉ. *Rev. métal.* 20, 481-9 (1923).—Discussion of the effects of each kind of blast. A. PAPIEHAU-COUTURE

Variation in coke consumption and determination of the cost of raw materials in blast furnaces making Thomas iron. P. PRESLES. *Rev. métal.* 20, 457-68 (1923).—Mathematical. A. PAPIEHAU-COUTURE

Lime vs. limestone in basic open-hearth practice as affecting cost of materials. L. M. FULTON. *Iron and Steel of Canada* 6, 158-9 (1923).—In the using of CaCO₃ the CO₂ evolved acts as a substitute for ore and no ore is required. With burned lime ore is required and this acts as a further source of metal. From these two reasonings calcs. are offered showing that the use of lime becomes cheaper than limestone. W. A. MUELLER

The calculation of the heat requirements of the Siemens-Martens furnace. HUGO BANSÉN. *Stahl u. Eisen* 43, 1031-39 (1923).—The primary formula suggested for the heat balance of the furnace is $(W + W_p) + (W_s + S_s - S_b) - R_1 = N - A + B + S_0 + R_2 + S_{b1} + S_{s1} + W_k + E$, in which W is the heat due to calorific value of the gas, W_p the sensible heat of the gases, W_s the heat of formation included, S_s the loss through the furnace, S_b the loss through the burners, R_1 losses due to incomplete combustion, N the total heat from the iron, melting, slag and super-heat, A the heat liberated by the slag formation, B the heat of formation, S_0 the wall loss of the working chamber, R_2 the radiation losses through the doors, gases and joints, S_{b1} the heat lost during the tapping period, S_{s1} the losses from the inner chamber, W_k the checker losses and E the chimney losses. This formula is then further simplified by substitutions and equalities under varying conditions of operation and fuels used. Charts are compiled for various capacity furnaces and the heats for slags, etc., are taken from these charts. The flow of the heat through the furnace walls is represented by a curve which indicates that the arithmetic av. of the thickness of the wall cannot be taken for the temp. calcn. The fuel used for the furnace must be taken into consideration; the available heat in each case varies and therefore must be detd. The type of gas used detd. the preheating required for the gas and air and also the amt. of the gas to be used. The rate of heating the furnace and the relation to size are also discussed, the various losses for different conditions are taken up and tables given for the losses at different parts of the furnace with a 42-ton type. Formulas are also discussed by which the various losses can be computed for the calcs. W. A. MUELLER

Electrolytic iron and its application. A. BOUCHAYER. *Rev. métal.* 20, 434-8 (1923).—Description of the properties of "Bévé" electrolytic Fe as produced commercially by the Etablissements Bouchayer & Viallet, Grenoble, and of its use. Compn.: C 0.029, Si 0.004, S 0.0048, P 0.0037, Mn 0.00, Pb 0.02-0.20, Cu 0.02-0.10%. An ingot obtained by fusion of electrolytic Fe scrap showed C 0.09, Si 0.089, S 0.01, P 0.07, Mn 0.072%. The crude and annealed Fe gave resp.: tensile strength 80, 29.7 kg. per mm.²; elastic limit 76, 18.3 kg. per mm.²; elongation 3, 40%. A. PAPIEHAU-COUTURE

Aluminium amalgam. I. FOGH. *Kgl. Danske Videnskab. Selskab. Math.-fys.*

medd. 3, No. 15, 6 pp. (1921).—Hg was sepd. from Al amalgam by centrifugation under oil and the remaining Hg removed by sublimation. The matt gray residue was not altered by the latter treatment. The residue consisted of a mass of fine needle-shaped crystals. The compd. had a mol. ratio of 4-5 Al:1 Hg. Much larger crystals were secured by very slow cooling. In this case the alloy contained 50% Al, or a mol. ratio of 7-8 Al:1 Hg. The hot satd. soln. of Al in Hg contained 0.38 g. Al per 100 g. At room temp. the Al content was only 2 mg.

Covering rails with manganese steel. ROUX. *Rev. métal.* 20, 490-2(1923).—Railway switches and diamonds are now covered with Mn steel (about 11% Mn and 1% C) by arc welding with an electrode of Mn steel (13.8% Mn and 1.23% C), and can be refilled when worn down. Adherence is improved by drilling holes (about 5 mm. in diam.) at an angle into the rail. A thin layer of martensite is formed at the surface of the two metals.

Progress shown in soaking pit design. ANON. *Iron Age* 117, 409-10(1923).
L. T. FAIRHALL
A. PAPINEAU-COUTURE
E. J. C.
Magnesium and extra-light alloys. A. PORTEVIN. *Rev. métal.* 20, 428-34(1923).—A review of the properties, uses and merits of Mg and its alloys.
A. P.-C.

Concentration of minerals. W. O. BORCHERT. *Can.* 233,601, Aug. 14, 1923. The flotation of minerals associated with colloidal matter in a pulp is improved by first scng. the colloidal matter from the pulp by overflow or decantation and then subjecting the pulp to a flotation operation. Na_2SiO_3 is used to cause the dispersion.

Metallurgical processes. J. A. KJOLBERG. *Can.* 233,245, Aug. 7, 1923. A finely powdered ore is mixed with a gas in a mixing chamber. The mixt. is kept in a whirling motion and projected into a heated reaction chamber through constricted discharge openings. App. is specified.

Recovering metals contained in metaliferous ore, waste residues or alloys. H. BARDT. *Can.* 233,566, Aug. 14, 1923. Metals are dissolved from ores, mats or alloys with dil. H_2SO_4 contg. a quantity of HNO_3 equiv. to the metal to be dissolved, under pressure greater than atm. The metals may then be recovered electrolytically.

Recovering light metals from scrap. A. BEBELSTEIN. *Can.* 233,132, July 31, 1923. Such metals as Mg and Al are recovered from scrap by moistening the scrap with MgCl_2 corresponding approx. to the quantity of impurities present and sufficient to ensure the agglutination of foreign substances. The scrap is melted and then moistened with fused MgCl_2 to cause agglutination of the impurities; the mass is stirred until all the MgCl_2 is taken up and allowed to settle and the metal melt is sepd. from the impurities.

Copper metallurgy. E. ERDOS. *Can.* 233,728, Aug. 21, 1923. Ground Cu ore is roasted and treated with a soln. of $\text{Al}_2(\text{SO}_4)_3$. When basic salts of Cu and Al are formed H_2SO_4 is added periodically until the Cu is completely extd. from the ore.

Treatment of copper ores. W. G. PERKINS. *Can.* 233,554, Aug. 14, 1923. Ores contg. CuS are crushed and roasted with access of air at $350-700^\circ$ to convert the CuS to CuSO_4 with a corresponding swelling, the oxidized material is heated with a reducing gas to reduce the CuSO_4 without melting and without fritting the gang so that the reduced material is obtained in a porous condition and then leaching the product with an NH_3 solvent of Cu in the presence of O.

Roasting sulfide ores. F. G. BREYER, J. P. HUBBELL and D. M. KERR. U. S. 1,463,867, Aug. 7. Sulfide ore, e. g., Zn ore, in finely divided form is agglomerated into lumps and passed progressively through a desulfurizing zone in contact with air a portion at least of which is preheated.

Desulfurizing zinc ore. W. L. MAXSON. U. S. 1,463,901, Aug. 7. Zn sulfide ore is sintered by heat derived from burning of sulfurous compds. in the charge of ore and the sintered product is roasted in lump form further to eliminate S.

Dissolving values from ores and similar materials. W. F. GORDON and E. W. KERRY. U. S. 1,464,036, Aug. 7. "Gas house liquor" is used as a solvent for dissolving Zn values or other values from ores or concentrates which may contain oxides, carbonates, sulfates and sulfites.

Reducing ores. J. H. REID. *Brit.* 192,426, Aug. 2, 1921. The ore is partially reduced by coking a finely divided intimate mixt. of ore, coal or the like and a flux, such as limestone, until the tarry constituents are removed and the coal is completely coked and without material calcination or decompn. of the limestone. The coked mixt. is charged hot into a blast furnace where it is smelted. Before coking the mixt. comprises 100 parts ore, 80 parts of bituminous coal and 40 parts of limestone, and after coking, 100 parts ore, 60 parts coke and 40 parts of practically unchanged limestone. The gases from the coking

retorts and the blast furnace are conducted to an hydraulic main as well as the usual purifiers and scrubbers before passing to a gas holder.

Iron manufacture. R. FRANCOY and K. P. McELROY. Brit. 191,764, July 14, 1921. A portion of the hot reducing gases is diverted from the blast furnace at a level below the usual top outlet; it may be cooled and returned in part to a higher zone of the furnace. The vol. of gases diverted is so adjusted in relation to the gases ascending the shaft that either a substantial net deposition of C is obtained within the shaft or the vol. ratio of CO to CO₂ in the top exit gases is not greater than 60 to 40 or the temp. of the exit gases is not greater than 250°. By regulating the proportions of the ascending and diverting gases the temp. of the blast may be reduced, its vol. increased to an amt. exceeding 70 cu. ft. per lb. of C charged into the furnace, and the accumulation of salines in the hearth prevented, these being carried away by the diverted gases. The vol. of gases diverted may be increased to lower the temp. and increase the ratio of CO₂ in the top gases and decreased to raise the temp. and decrease the CO₂ ratio. Some of the heat obtained from the diverted gases may be used to heat the air blast or for other purposes.

Basic steel. R. BAURET. U. S. 1,464,634, Aug. 14. Hard steel with a high C content and practically dephosphorized is produced in a basic converter by prep. in the converter, before the pig Fe is added, a liquid bath comprising lime and oxides such as those of Fe and Ca which effect rapid dephosphorization of the pig Fe. Cf. C. A. 17, 2882.

Desulfurizing iron and steel. D. D. JACKSON, J. D. SEARS and F. CONLIN. Can. 233,301, Aug. 7, 1923. Fe, steel, iron alloys and Cu are desulfurized by treating the molten metal with a mixt. of alkali metal silicate, hydroxide or carbonate.

Ferro-chromium. W. L. TURNER. Brit. 192,741, Oct. 12, 1921. Low-carbon Fe-Cr is made from chrome-iron ore by a thermo-aluminic process carried out in an elec. furnace, whereby the addn. of other oxidized materials is rendered unnecessary. A metal bath may be first melted in the furnace and covered with a fusible slag, the bath is subjected to an elec. current and there is then added thereto a mixt. of chrome iron-ore and Al. Cf. 123,103 (C. A. 13, 1444) and 191,167 (C. A. 17, 3013).

Alloys. P. DE MILES. Brit. 191,918, Dec. 7, 1921. An alloy is composed of 60-70% of a silico-nickel contg. 1-5% of silicon, 12-15% of a ferro-manganese contg. 20-25% of Mn, 1.5-2.5% of C, 3-5% of W, and substantially all the remainder Cr. The Ni may be wholly or partly replaced by Co and the W by Mo. During manuf., a small quantity of Al may be added a trace of which remains. An av. alloy may contain 10.64% of Fe, 1.64% of C, 0.02% of Al, 82.2% of Ni, 1.73% of Si, 17.65% of Cr, 3.73% of W, and 2.42% of Mn.

Improving the electric conductivity of alloys. METALLBANK UND METALLURGISCHE CHS. AKT.-GES. Brit. 192,414, Jan. 27, 1923. The elec. cond. of Al alloys contg. no Mg, Al alloys contg. up to 20% of Cu, Zn, Be or Li, Cu alloys contg. up to 15% of Al or Sn, Cu-Zn alloys contg. up to 50% of Zn, Mg alloys contg. up to 25% of Al, Zn or Cu and alloys of Fe and C is improved by heating the alloys to a temp. depending on their compn., then bringing them to a lower temp. either by cooling or by quenching and reheating, and maintaining them at the lower temp. for some time. In an example, an Al alloy contg. 4% Cu and 10% Zn is heated to a temp. of 480°, cooled to 150° or quenched and reheated to 150° and maintained at the latter temp. for some time.

Air-hardening steel alloy. W. F. FINKL. U. S. 1,464,174, Aug. 7. A steel alloy contg. C 0.50-0.85, Cr 0.40-0.95, Mo 0.30-0.80 and Ni 0.50-2.00% is adapted for machine parts which are air-hardened during heat treatment.

Electrical resistance alloy. F. A. FAHRENWALD. U. S. 1,464,312, Aug. 7. An alloy for elec. resistances highly resistant to corrosion is formed of Fe together with Cr 10-25% and 1-5% of Ti or Zr.

Apparatus for amalgamating metals. D. L. PENROD. U. S. 1,464,293, Aug. 7.

Prevention of corrosion of steel ropes. A. GORDON and T. S. JOLLY. Brit. 192,179, Nov. 1, 1921. A method of preserving steel ropes, which are liable to corrosion especially in the presence of acid water, consists in applying to the rope a mixt. of powdered Zn or other metal electronegative to iron and a grease incapable of ionic dissociation, the term "electronegative" being used with reference to the current set up in the external circuit of a couple. Suitable greases are the semi-solid mixts. of paraffins or olefins. The corrosive fluid attacks the Zn only, while the Fe of the rope is preserved.

Welding metals. PREMIER ELECTRIC WELDING CO., LTD., and J. H. PATERSON. Brit. 191,910, Nov. 30, 1921. In order to produce a reducing atm., the coating of an Fe or Fe-alloy electrode for welding Fe or steel contains the carbonate of a heavy metal or metals, the oxides of which have a comparatively low m. p., and C or carbonaceous material. The coating may comprise Fe, Ni or Mn carbonate, and coke or anthracite.

Mixts. are also described comprising chalk, ferrous, nickel or manganous carbonate, and lamp black; and ferrous and manganous carbonates and lamp black, resp. The outer electrode coating, which may be colored, is made of pptd. chalk bound with glue or silicate of soda, and may contain a reducing agent such as dextrin.

Welding nickel, etc. ALLEN-LIVERSIDGE, LTD., and C. COULSON-SMITH. Brit. 192,193, Nov. 4, 1921. Ni and alloys contg. a high % of Ni are welded in the presence of C or carbonaceous material which produces a reducing atm., reduces the rate of cooling, and prevents disintegration of the substances. Bars of Ni with chamfered ends are welded together on a C block with a Na_2SiO_3 flux. The welded bar may be annealed, hammered, or rolled. The longitudinal seam of a tube is effected by the insertion of C rods. In lieu of the blowpipe, the weld may be effected by C electrodes in direct contact with the metals, or by carbon-covered electrodes.

Electrodes for soldering, etc. E. H. JONES and ALLOY WELDING PROCESSERS, LTD. Brit. 192,852, Dec. 1, 1921. An electrode for soldering or depositing metal by the elec. arc is coated with a paste consisting of a carbonate of an alk. earth or earths such as CaCO_3 and BaCO_3 and fluorspar in approx. equal parts, mixed with a soln. of a sol. silicate, for the purpose of preventing the formation of blow holes and flaws in the deposited metal. The CaCO_3 and the fluorspar are ground to powder and mixed together, with or without a proportion of BaCO_3 equal to 10% of the fluorspar, sufficient Na or K silicate in soln. (50° Twaddell) being added to form a creamy paste.

Material for bearings. R. G. GUPPILL. U. S. 1,464,569, Aug. 14. Graphite or similar material is embedded in the surface of bearing metal such as alloys of Pb and Sb in order to reduce friction in use.

Type metal. S. BRUSA. Brit. 191,814, Oct. 15, 1921. Type for printing characters, margins, vignettes, or the like are cast from an alloy having a Zn base, the metal being injected into the mold by the agency of fluid under pressure. The alloy may consist of 90% of Zn and 10% of Al. A small % of other metals, such as Cu, Sn, and Ni, may be added to increase the hardness.

10—ORGANIC CHEMISTRY

CHAS. A. ROULLER AND CLARENCE J. WEST

Dependence of rotatory power on chemical constitution. XX. The rational study of optical properties including refraction. HAROLD HUNTER. *J. Chem. Soc.* 123, 1671-82(1923); cf. *C. A.* 17, 1949.—H. indicates the pressing need for dealing with the question of dispersion in an adequate manner and suggests and correlates some dispersion equations in an attempt to prep. the way for the satisfactory soln. of the problem of optical dispersion as applied to natural rotatory power, refractive index and magnetic rotatory power. The dispersion equations which appear most suitable for application to org. compds. are Sellmeier's equation for refractive dispersion, Drude's equation for natural rotatory dispersion and Drude's equation for magnetic rotatory dispersion (which should contain a term independent of the absorption). Refractive power is much more constitutive than has hitherto been supposed. The accepted methods of calcn. are shown to be inadequate and even harmful, because they have conferred on this property an appearance of additivity which is as misleading as it is false. The proposed dispersion equations demonstrate clearly the connection between the 4 optical properties: Natural and magnetic rotatory powers, refractive index and absorption spectrum. The original should be consulted for the equations and discussion.

C. J. WEST

Electrosynthesis in organic chemistry. JAMES WALKER. *Proc. Roy. Inst. Cl. Britain* 1921, 3 pp.—An abst. of a lecture in which the possibilities of electrosynthesis are emphasized. The fact that it is not more extensively used is probably in part due to the care which must be exercised in adjusting the phys. conditions in order to secure a successful result.

C. J. WEST

Electrolytic oxidation and reduction phenomena in organic chemistry. M. LE-MARCHANDS. *Ann. energie* 11, 225-30(1922); *Chimie et industrie* 9, 1180(1923).—The formation of hydrocarbons by electrolysis of acids (C_2H_4 from AcOH) is thought to involve intermediate production of peroxides, which would explain the impossibility of obtaining $\text{C}_2\text{H}_4(\text{NH}_2)_2$ from glycochol. Nitrotoluenes give the corresponding alcs. and aldehydes, which can be transformed into the acids. *o*- $\text{MeC}_6\text{H}_4\text{SO}_2\text{NH}_2$ has given up to 75.4% saccharin in presence of Na_2CO_3 . Electrolysis of PhOH gives *o,p'*-dihydroxydiphenyl and (*p*- HOCC_6H_4)₂, which are ultimately transformed into hydroquinol

and pyrocatechol. The 2nd diphenol can even be transformed into fumaric acid. The process of oxidation of cresols is similar; but *p*-cresol also gives (5,2-Me(HO)C₆H₃)₂O, m. 196°. MeOH and EtOH give H and CH₄, resp., on electrolytic oxidation. Electrolytic oxidation of the leuco-base of malachite green in the presence of U nitrate as catalyzer does not give any results of com. importance. (*p*-HO₂SC₆H₄)₂S₂ is oxidized to C₆H₄(SO₃H)₂.

A. PAPIERAU-COUTURE

Production of pure trichlorethylene. SVEN BODFORSS. *Tidsskrift for Kemi og Bergvaesen* 2, 87-8(1922).—Some samples of C₂HCl₃ show a great changeability and are very soon decompd. by the air even in the dark into HCl, CO, COCl₂ and CHCl₂COCl, while most samples will not show this tendency. B. has examd. such a decomposable sample by very careful fractional distn. and found a very const. b. p. He draws the conclusion that a possible catalyzing contaminating substance should have a similar b. p. and be present in very small amts. He tried to remove this substance by chem. means and found that by shaking the sample several times with H₂SO₄ (d. 1.675), and removing the acid by washings with water he obtained a clear colorless liquid of pleasant odor that kept as well in the dark as the usual com. samples. In daylight C₂HCl₃ is rapidly decompd. by the air in all cases.

CHR. H. A. SYVERTSEN

Correction to our work: "Judging and dehydration of methanol with the aid of magnesium." NIELS BJERRUM AND LASZLO ZECHMISTER. *Ber.* 56B, 1247(1923); cf. C. A. 17, 2701.—The cond. of picric acid at 25° in MeOH dehydrated with Mg has been found to be 12.62-12.83, in good agreement with the value (12.74) given by Goldschmidt and Thuesen for alc. dehydrated with Ca.

C. A. R.

Conversion of methyl chloride to methanol. II. RALPH H. MCKER AND STEPHEN P. BURKE. *Ind. Eng. Chem.* 15, 788-94(1923); cf. C. A. 17, 2701.—The secondary reactions involved in the formation of MeOH by the action of MeCl and steam are investigated. An exhaustive study of the reactions: CaCl₂ + H₂O → Ca(OH)₂ + 2HCl, CaCl₂ + 2MeOH → Ca(OH)₂ + 2MeCl, MeOH + HCl → MeCl + H₂O, MeOH + MeCl → Me₂O + HCl, of the pyrogenetic decompn. of MeOH and of MeCl, the conditions influencing the reaction, such as the size and structure of the Ca(OH)₂ granules, the velocity of the flow of gas, the temp., the partial pressure of H₂O vapor, inert gas and the material of the app., indicate that the most advantageous method for converting MeCl to MeOH is to pass MeCl mixed with steam over highly porous granular Ca(OH)₂ at 350°, giving a yield of approx. 98% MeOH + Me₂O (Me₂CO-free). The relative amts. of MeOH and Me₂O depend on the partial pressures of MeCl and steam. Curves show the relative yields. Any Me₂O formed may be converted to MeOH by a catalytic process which consists essentially in catalyzing the reaction: Me₂O + H₂O → 2MeOH by Al₂O₃ (cf. *Compt. rend.* 148, 1735(1909); *Ann. chim. phys.* 20, 298, 343(1910)).

C. C. DAVIS

The tertiary methyleptenols. I. Their ketonic decomposition. V. GRIGNARD AND R. ESCOURROU. *Compt. rend.* 176, 1860-63(1923).—Certain secondary and tertiary alcs. have a tendency to decomp. with the formation of an aldehyde or a ketone. G. and E. studied this reaction in the case of the tertiary unsat. methylheptyl alcs. They were prepd. from 3 different sources. In each case there was isolated 1st a mixt. of the corresponding ketones, an α-form CH₃:CMeCH₂:CH₂:CH₂:COMe and a β-form, Me₂C:CHCH₂:CH₂:COMe. This was converted into the alc. by the well known Grignard reaction. Above the alcs. there was found frequently a small quantity of a yellowish liquid, C₁₀H₁₈O, to which is assigned the constitution Me₂C:CHCH₂:CH₂:CMe:CAcCH₂:CH₂:CMe₂. In the case of these alcs. the ketonic decompn. takes the form Me₂C:CH-CH₂:CH₂:CMe(OH)R → Me₂C:CHCH₂:CH₂:COMe + RH. The extent of the reaction depends on R. If the latter is Me or Et it is very small, but increases with the size of R. If R is secondary it is more pronounced. Me₂C:CHCH₂:CH₂:CMe(OH)CHMe₂ is decompd. 75% even under 12 mm. Satd. alcs. do not show much sign of this reaction. A trace of acid or alkali catalyzes the reaction, as does colloidal Pt in the case of the satd. alcs.

ROGER G. FRANKLIN

Hydrolysis of the sulfoxide and the sulfone of β,β'-dichlorodiethyl sulfide. A. E. CASHMORE. *J. Chem. Soc.* 123, 1738-45(1923).—(ClCH₂CH₂)₂SO and NaOH in 95% EtOH yield β,β'-diethoxydiethyl sulfoxide (I), pale yellow, viscous liquid, b₂₅ 177-9°. In H₂O the product of reaction is apparently 1,4-thioxan sulfoxide (II), b₁₅ 147°, m. about 25°. In 50% EtOH the reaction product is a mixt. of I, II and β,β'-dihydroxydiethyl sulfoxide, dark yellow, viscous liquid, b₂₅ 295-10°. NaOH and (ClCH₂CH₂)₂SO₂ in 95% EtOH yield β,β'-diethoxydiethyl sulfone, pale yellow, b₁₅ 242-4°. The corresponding di-MeO deriv. b₂₅ 192° and the diisooamyl oxy deriv. (III), b₁₅ 222°. In H₂O 1,4-thioxan sulfone results. In 50% EtOH a mixt. of the above 2 products results. Aq. NaOH has no action on (HOCH₂CH₂)₂S. None of these derivs. has

vesicant action and they are of little physiol. importance, though III has a nicotine-like action in that it paralyzes the whole autonomic nervous system, but it differs from nicotine in that there is no preliminary stimulation. C. J. WGRS.

The action of silver nitrate on iodoethylene and the properties of dinitroethane. A. V. IPATOV. *J. Russ. Phys. Chem. Soc.* 49, 297-317(1917).—*Prepn. of dinitroethane.*—To 75 g. CH_2I in 300 cc. of dry ether in a flask with a reflux leading to a Brabsorption bottle was added dry and finely powdered AgNO_3 . The reaction is exothermic. After 2 days fresh portions of AgNO_3 were added and the mixt. was heated on a water bath for 4 hours, filtered and washed the AgI with dry ether. The sirupy product after evapn. of the ether was dried over H_2SO_4 . Wt. 58 g. The wash bottle contained $\text{CH}_2\text{:CHBr}$. The reaction product was fractionated under reduced pressure. Fraction I, b_p 70-2°; II b_p 72-8°; III b_p 81-106°. The residue in the flask was reworked with AgNO_3 . Fraction II was refractionated; analysis and mol. wt. and mol. vol. detns. showed it to be dinitroethane, acid to litmus, b_p 94-6°, stable to heat and keeps well, d_{20} 1.4602; $(\text{CH}_2\text{NH}_2\text{HCl})_2$ is formed by reduction with Zn and HCl. $\text{C}_2\text{N}_2\text{O}_4\text{Br}_2$ obtained by bromination by the Victor Meyer method, m. 46-7°. GEORGE W. PUCHER

Bromotrinitromethane. II. ERICH SCHMIDT, RICHARD SCHUMACHER AND RICHARD ASMUS. *Ber.* 56B, 1239-42(1923); cf. *C. A.* 17, 381.—In connection with the study of the addn. of esters of HOBr to olefin double bonds by means of $\text{CBr}(\text{NO}_2)_2$ in alc. it was noted that with products contg. labile halogen the working up of the reaction mixt. with alkalis is unsuccessful. These have now been replaced by $\text{K}_4\text{Fe}(\text{CN})_6$ in AcOH . Instead of alics., other HO compds., such as acids (especially HCO_2H) may be used: $-\text{CH}_2\text{CH}- + \text{HCO}_2\text{H} + \text{CBr}(\text{NO}_2)_2 = -\text{CH}(\text{O}_2\text{CH})\text{CHBr}- + \text{CH}(\text{NO}_2)_2$. *Bromomethoxyhydrindene*, faintly yellow, b_p 98°, is obtained in 4.5 g. yield from 6.3 g. $\text{CBr}(\text{NO}_2)_2$, dropped into 3.2 g. indene in 20 cc. cold MeOH , allowed to stand 12 hrs. at room temp., heated 1 hr. on the H_2O bath, treated with H_2O and satd. NaCl and extd. with Et_2O , the ext. then being kept 24 hrs., with frequent shaking, over 11.5 g. crystd. $\text{K}_4\text{Fe}(\text{CN})_6$ in 50 cc. H_2O and 6.5 cc. of 50% AcOH , poured off from the aq. layer and again treated in the same way with 5.7 g. $\text{K}_4\text{Fe}(\text{CN})_6$ and 3.2 cc. AcOH . *O-Formyl-2-bromo-1-cyclohexanol*, $\text{C}_6\text{H}_{10}(\text{O}_2\text{CH})\text{Br}$ (29 g. from 18 g. urea, 46 g. $\text{CBr}(\text{NO}_2)_2$) and 50 cc. cold HCO_2H allowed to stand 12 hrs. with 16.4 g. cyclohexene and then treated as above with $\text{K}_4\text{Fe}(\text{CN})_6$, b_p 68-9°; 8 g. in 80 cc. MeOH allowed to stand 18 hrs. with 8 cc. HCl (d. 1.19) gives 5.9 g. *2-bromo-1-cyclohexanol*, b_p 60-1°. *α-Formyloxy-β-bromopropylbenzene*, obtained in 69.4% yield from PhCH:CHMe , b_p 104°. *O-Formylcamphene bromohydrin*, $\text{C}_{10}\text{H}_{16}(\text{O}_2\text{CH})\text{Br}$ (yield, 73.5%), b_p 109-11°. C. A. R.

Influence of hydrogen chloride on the enolizing action of Grignard's reagent. V. K. BHAGWAT. *J. Chem. Soc.* 123, 1803-7(1923).—B. and Sudborough (*C. A.* 14, 1674, 3231) found that simple aldehydes and ketones display very little tendency to enolize in the presence of Grignard's reagent but a moderately high degree of enolization was observed in the case of an acid sample of MeEtCCHO ; it was suggested that this result might have been due to the enolizing action of acid. A further study of the action of Grignard's reagent upon AcMe , EtCHO and MeEtCCHO in Am_2O and in the presence of AcOH and HCl showed that AcOH has no effect on the enolizing action of Grignard's reagent owing to decompn. immediately consequent on its exposure to the attack of the reagent but that HCl exerts a great influence on the enolization of these aldehydes and AcMe , the degree of enolization being proportional to the quantity of acid present. C. J. WGRS

The oxidation of hydrocarbons with special reference to the production of formaldehyde. III. The action of oxygen on mixtures of methane and ethylene and their oxidation products. T. S. WHEELER AND E. W. BLAIR. *J. Soc. Chem. Ind.* 42, 260-2T, 263-6T(1923); cf. *C. A.* 17, 1950.—A study of the interactions occurring after a certain degree of oxidation of hydrocarbons, when O, hydrocarbon and oxidation products are all present. The important reactions have already been studied singly (cf. *J. Chem. Soc.* 81, 537(1902)) but not simultaneously. The app. was that used for CH_4 and C_2H_4 (cf. *C. A.* 17, 58). Coal gas, which approximates the condition required, was used for the expts. by dilg. with O and with N to increase its explosive range. The results explain the action of O for a brief time on a mixt. of a hydrocarbon and its oxidation products. As the temp. rises, first one and then another constituent begins to interact, and the rates of interaction increase rapidly until they reach a const. ratio to one another. A comparison of these rates shows why CO and H_2O are the chief products of the slow oxidation of CH_4 under conditions in which HCHO decomp., for at these temps. and times of heating, H is first attacked, next CH_4 and then CO. The rapid increase at high temps. in the rate of oxidation of CO explains the presence of CO_2 in the products at such temps. The rate of oxidation of the hydrocarbon is not greatly

affected by the presence of intermediate products, though these dil. the reaction mixt. The yield of HCHO in this series of expts. was slightly lower than that obtained with CH_4 . Decompn. of HCHO may also be induced by simultaneous oxidation of H. The yield indicates the same regularities as those with CH_4 previously described and the same conclusions apply. The influence of catalysts and surfaces was also studied. At low temps. the decompn. and oxidation of intermediate products (including HCHO) were more accelerated by pumice than oxidation of the hydrocarbons, but at high temps. the rate of oxidation increases so that H and CO accumulate. The yields of HCHO were similar to those from C_2H_4 . With Fe_2O_3 , similar results were obtained. The acceleration of oxidation of intermediate products (H and CO) at low temps. is due in part to reduction of the Fe_2O_3 and its reoxidation by O, whereas the oxidation of the hydrocarbons is due chiefly to surface action. Much Fe_2O_3 was reduced at the end of the expt. It is suggested that this be made the basis of a partial combustion method of gas analysis, H and CO being first burned by Fe_2O_3 and the CH_4 then analyzed as usual. The partial combustion and detn. could be done in a circulation app., the fall in pressure due to oxidation of H and CO being noted and CO_2 then absorbed by KOH and a sample of the circulating gas could then be exploded. With Hg, oxidation of C_2H_4 , CO and H was accelerated, but not of C_2H_2 , the catalytic effect being small, probably because of its small surface. The yield of HCHO was high compared with that from Fe_2O_3 and pumice. The direct decompn. of HCHO induced by catalysts is probably a surface action. In all expts. the great diln. of the C_2H_4 prevented its thermal decompn.

C. C. DAVIS

Hexamethylenetetramine. RUDOLF PUMMERER AND JOSEF HOFMANN. *Ber.* 56B, 1255-9(1923).—Hexamethylenetetramine (I) takes up no H in H_2O at room temp. in the presence of Pt, which indicates that it does not contain double bonds as in some of the formulas which have been suggested for it. Almost all previously published mol. wt. detns. on I are somewhat lower than the calcd. P. and H. have now also obtained low values in freezing H_2O (generally about 120 instead of 140) and these values are entirely independent of the concn. (from 1 to 15%) of the I. Although I is generally considered a strong base it does not redden phenolphthalein and its cond. is exceedingly small; assuming that the cond. of the cation is negligible as compared with that of the OH ion, i. e., that λ_∞ of the base = the migration velocity of the HO ion, the dissociation const. of the base comes out 2×10^{-8} with reasonable constancy from the condl. measurements. The phenol addn. products of I were also studied. The cresolates are obtained quant. and instantaneously at room temp. by rubbing the components with a few drops of alc.; they show the same properties as the compds. prepd. by Harvey and Buckeland by long heating on the H_2O bath (*C. A.* 15, 831). In both H_2O and C_6H_6 the triphenolate and the *o*-cresolate are almost completely dissociated into their components. The cond. of a soln. of 1 equiv. each of I and PhOH, however, showed distinct salt formation. By the same approximation method as above the dissociation const. of I is found to be about 10 times that of the monophenolates, 100 times greater than that of PhOH, and the cond. of the triphenolate is even greater.

C. A. R.

Action of formic acid on ethylglycerol—transformation into β -ethylacrolein. RAYMOND DELABY. *Compt. rend.* 176, 1898-1901(1923).—Ethylglycerol was boiled for 6 hrs. with 2.5 times its wt. of crystd. HCO_2H and distd. The main fraction, a mixt. of mono- and di-formates and unchanged ethylglycerol, b_p 150-2°. The residue which solidified at 60-1° is the triformate. On heating the distillate to 270° there pass over water, HCO_2H and 2 unsatd. isomeric alcs. $\text{CH}_2\text{:CHCH(OH)Et}$ and β -ethylalyl^{ulc.}, b. 139-40°, previously unknown. These products were identified by the usual means. The $\text{EtCH:CHCH}_2\text{OH}$ on oxidation with CrO_2 gives β -ethylacrolein, b. 126-30°, also previously unknown.

ROGER G. FRANKLIN

Mechanism of the pinacol-pinacolin and Wagner-Meerwein transformations. C. K. INGOLD. *J. Chem. Soc.* 123, 1706-13(1923).—The rearrangement of the C skeleton which so frequently accompanies the dehydration of tert-alkylcarbinols is viewed as involving the formation of an intermediate cyclic compd., which is supposed to be formed by the elimination of H_2O and to undergo subsequent fission in such a way as to give rise to the altered C skeleton. There is no evidence that the intermediate ethylene oxide would undergo the isomeric change postulated and it is further difficult to apply it to some of the transformations in the terpene series. An alternative explanation has been offered by Robinson (*C. A.* 16, 2243). Decisive evidence in favor of R.'s views, so far as concerns the character of the ultimate product of the change, has been obtained by the oxidation of the hydrocarbon, C_8H_{16} , prepd. from $(\text{CH}_2)_2\text{:C}(\text{CH}_2\text{Br})_2$. According to the older views, the 3 possible formulas for C_8H_{16} are $\text{CH}_2\text{:CH:CCH}_2\text{CH}_2$, $(\text{CH}_2)_2\text{:C:}$

CHCH_2 and $(\text{CH}_2)_2$: $\text{CHCH}:\text{CH}_2$. According to Robinson, they are: $\text{CH}_2\text{CH}_2\text{CH}_2\text{C}:\text{CH}_2$, $\text{MeC}:\text{CHCH}_2\text{CH}_2$ and $\text{MeCH}:\text{CH}:\text{CH}_2$. The oxidation products of the hydrocarbon (15 g.) are: levulinic acid (9.3 g.), glycol, $\text{C}_6\text{H}_5(\text{OH})_2$ (3.6 g.), $(\text{CO}_2\text{H})_2$ (3 g.) and $(\text{CH}_2\text{CO}_2\text{H})_2$ (3 g.). The theoretical oxidation product of $\text{MeC}:\text{CHCH}_2\text{CH}_2$ is levulinic acid, or $(\text{CH}_2\text{CO}_2\text{H})_2$, as the ultimate product.

Nitriles of olefinmonocarboxylic acids. K. v. AUWERS (with O. JORDAN, TH. MEISSNER AND O. SEYDEL). *Ber.* 56B, 1172-85(1923).—Lespieau has shown with certainty (*Bull. soc. chim.* [3] 33, 55(1905)) that the product obtained from allyl bromide or iodide and KCN is allyl cyanide (I), $\text{CH}_2:\text{CHCH}_2\text{CN}$, although it reacts as if it were the isomeric crotononitrile (II), $\text{MeCH}:\text{CH}_2\text{CN}$. Spectrochemically, I should be normal, while II, contg. a conjugation between the double and the triple union, should show optical exaltations. Eykman (*Chem. Weekblad* 3, 711(1906)) and Bruylants (*C. A.* 17, 2867) have already found that I is, as a matter of fact, optically normal, but as the phys. consts. they give differ in part, it seemed desirable again to study I. Pure I can be obtained only when certain precautions are observed. Especially disturbing is the great sensitiveness of I to alkalis, which easily convert it into II at room temp., and it is therefore better to use CuCN than KCN in its prepn. The allyl halide should also be pure, for if it contains any 1- or 2-bromopropylene, *e. g.*, these do not react with the CuCN and it is difficult to sep. them from the resulting crude I by fractional distn. Below are the consts. of an absolutely halogen-free prepn. of I: $d_4^{14.8}$ 0.8497, n 1.40626, 1.40868, 1.41511, 1.41996 for α , D, β and γ at 14.8°, EM -0.25, -0.27, -0.03 and -0.06 for α , D, β - α and γ - α , resp. The consts. of 2 samples of II prepd. from the aldoxime and Ac_2O and of I made from the amide and P_2O_5 differed; those of the last, which are intermediate between those of the first 2, are as follows: $d_4^{14.1}$ 0.8304, n 1.42104, 1.42488, 1.43361, 1.44103 at 14.1°, EM (mean for the 3 samples) 0.67, 0.69, 0.11, 0.20. Below are the most probable consts. for I, II and isocrotononitrile, resp. (the last taken from Bruylants): b. 118.5°, 120.5°, 107.5°; d_4^{20} 0.836, 0.824, 0.824; n_D^{20} 1.406, 1.425, 1.418; EE -0.36, 1.00, 0.78 for α ; -0.37, 1.022 0.79 for D; -8, 25, 20% for β - α ; -9, 30, — for γ - α . With the help of these data it is easy to follow the gradual rearrangement of I into II under the influence of alkalis; in an Et₂O soln. of I shaken at room temp. with a little NaOH, about 0.5 of the I is rearranged in 1 hr. and in about 24 hrs. is reached an end point when the mixt., judging from the optical consts., contains about 10% I and 90% II; if this were an equil. between the 2, it would be expected that it would also be reached starting from II, but a sample of II treated the same way was unchanged after 5 hrs. This sensitiveness of I to alkalis explains many of the contradictions found in the literature. To det. whether nitriles of Δ^1 - and Δ^2 -olefincarboxylic acids in general can be distinguished by means of their optical consts. a no. of homologs of each series were prepd.; below are the EE values for α , D, β - α and γ - α , resp.: MeCH:CHCN 1.00, 1.02, 25, 30; CH₂:CHCH₂CN -0.36, -0.37, -8, -9; EtCH:CHCN 1.01, 1.02, 23, 25; MeCH:CHCH₂CN 0.11, 0.10, 2, 5; EtCH:CHCH₂CN 0.13, 0.13, 4, 6; Me₂CHCH:CHCN 0.90, 0.90, 24, 26; Me₂C:CHCH₂CN -0.03, -0.04, 5, 7; Me₂CHCH₂CH:CHCN 0.98, 1.00, 23, 23; Me₂CHCH:CHCH₂CN 0.30, 0.30, 5, 5; Me(CH₂)₅CH:CHCN 0.54, 0.55, 15, 15. In view of the well known tendency to the formation of conjugated systems of multiple bonds wherever possible, aldehydes would be expected to react with $\text{NCCH}_2\text{CO}_2\text{H}$ according to the scheme $\text{RCH}_2\text{CHO} + \text{NCCH}_2\text{CO}_2\text{H} \rightarrow \text{RCH}_2\text{CH}(\text{OH})\text{C}(\text{CN})\text{CO}_2\text{H} \rightarrow \text{RCH}_2\text{CH}:\text{C}(\text{CN})\text{CO}_2\text{H} \rightarrow \text{RCH}_2\text{CH}:\text{CHCN}$. Braun (*Monatsh.* 17, 218(1896)) and Strassmann (*Monatsh.* 18, 722(1897)), however, obtained Δ^2 -nitriles with some of the higher aliphatic aldehydes. A no. of these condensation products have accordingly been prepd. and their structures detd. by the optical method, with the following results (values of EE for α , D, β - α and γ - α , resp.): MeC:C(CN)CO₂Et (III) 0.83, 0.85, 30, 29; MeCH:CHCN 0.72, 0.72, 17, 22; EtCH:C(CN)CO₂Et (IV) 0.80, 0.82, 30, 31; MeCH:CHCH₂CN (V) 0.11, 0.11, 2, 5; Me₂CHCH:C(CN)CO₂Et (could not be examd., owing to lack of sufficient material); Me₂C:CHCH₂CN (VI) -0.03, -0.04, 5, 7; Me₂CHCH₂CH:C(CN)CO₂H (VII) 1.35, 1.39, 41, 46; Me₂CHCH₂CH:C(CN)CO₂Et (VIII) 0.81, 0.83, 29, 30; Me₂CHCH:CHCH₂CN (IX) 0.30, 0.29, 5, 5. The nitrile acids are therefore Δ^1 -derivs. in which, in general, the double bond shifts when CO₂ is eliminated, with formation of a Δ^2 -nitrile. This is apparently not due to a rearrangement, at the high temps. at which the nitriles are obtained, of a Δ^1 -nitrile first formed, as the latter are as stable as their isomers at high temps. No

explanation can as yet be given of this apparently anomalous change of a conjugated into a non-conjugated system. Equally remarkable is the isolated position occupied by I; while it is rapidly isomerized to II by cold alkali and smoothly yields crotonic acid on hydrolysis, its homologs give almost exclusively the corresponding β,γ -olefinarboxylic acids, even after several hrs. boiling with alkali. The condensation of aldehydes with $\text{NCCH}_2\text{CO}_2\text{H}$ in general gave better yields when the components were heated 4 hrs. at 60–70° with 0.02 mol. piperidine (Knoevenagel, Ger. pat. 156,560). $\text{MeCH:C(CN)CO}_2\text{H}$, m. 80° (Fiquet, *Bull. soc. chim.* [3] 7, 767(1892), gives 92°); *Et ester* (III), obtained in 52% yield from the acid with alc. and concd. H_2SO_4 at 110°, b_{20} 112°, $d_4^{19.8}$ 1.0255, n 1.44988, 1.45302, 1.46172, 1.46888 for α , D, β and γ at 18.8°; the consts. of the nitrile, obtained in only 2 g. yield from 15 g. of the nitrile acid, indicate that it is a mixt. of much II with a little I. $\text{EtCH:C(CN)CO}_2\text{H}$, m. 82–4° (Strassmann gives 64–5°); *Et ester* (IV) (yield, 51%), b_{20} 121–2°, $d_4^{19.9}$ 1.0004, n 1.44988, 1.45292, 1.46152, 1.46869 at 19.9°; V (yield, 15%), b_{110} 85–7°, $d_4^{19.8}$ 0.8430, n 1.42397, 1.42650, 1.43374, 1.43968 at 18.8°. VI (yield, 18%), b_{11} 63°, $d_4^{19.8}$ 0.8556, n 1.43529, 1.43796, 1.44529, 1.45129 at 18.8°. VII, m. 53°, $d_4^{20.0}$ 0.9711, n 1.44367, 1.44690, 1.45599, 1.46409 at 99.6°, gives with O_3 in dry $\text{AcOEt Me}_2\text{CHCH}_2\text{CHO}$ almost exclusively: *Et ester* (VIII), b_{13} 121–2°, $d_4^{19.7}$ 0.9666, n 1.45198, 1.45502, 1.46340, 1.47037 at 19.7°. IX (2.5 g. from 15 g. VII), b_{11} 57–8°, $d_4^{21.3}$ 0.8241, n 1.42691, 1.42932, 1.43614, 1.44166 at 22.3°. gives Me_2CHCHO almost exclusively with O_3 and with boiling 10% KOH yields a product whose consts. indicate that it is a mixt. of Δ^1 - and Δ^2 -isoleptenic acids.

Derivatives of behenic and erucic acids. YOSHIYUKI TOYAMA. *J. Chem. Ind. Japan* 25, 1053–5(1922).—Me behenate m. 54–4.5°, b. 224–5°. Et behenate m. 50–0.5°, b. 230–1°. Behenamidine, m. 111–2°. Behenanilide, m. 101–2°. Me erucate is a nearly colorless liquid, d_{16} 0.8735, d_{20} 0.8702, n_{16} 1.4577, n_{20} 1.4558, b_{11} 221–2°. Et erucate is a nearly colorless liquid, d_{16} 0.8676, d_{20} 0.8648, n_{16} 1.4562, n_{20} 1.4543, b. 229–30°. Erucamide m. 82.5–83°. Erucanilide m. 65.5–66°. J. C. S.

1,2-Ethylene sulfides. MARCEL DELEPINE AND SIMON ESCHENBRENNER. *Bull. soc. chim.* 33, 703–11(1923).—Four examples of this type in the acyclic series are known: $\text{CH}_2\text{CH}_2\text{S}$, $\text{MeCH}_2\text{CH}_2\text{S}$, $\text{EtCH}_2\text{CH}_2\text{S}$ and $\text{Me}_2\text{C}(\text{CHMe})\text{S}$. The first on oxidation

with HNO_3 gave as primary product $\text{HSO}_3\text{CH}_2\text{CO}_2\text{H}$, but among the condensation products was $\text{HSO}_3\text{CH}_2\text{CH}_2\text{S}(\text{CH}_2)_n\text{CO}_2\text{H}$, both being identified by analysis of the Ba and K salts. With AcOH , NH_3 , $\text{C}_2\text{H}_5\text{N}$, AgNO_3 , no primary products but only condensation products were obtained. With HCl in traces, $\text{CH}_2\text{CH}_2\text{S}$ yielded a white

amorphous product, but when added to HCl in excess (3 parts) with cooling the products were: I $\text{HS}(\text{CH}_2)_n\text{CH}_2\text{Cl}$, b_{11} 43°, b_{20} 60°, d_4^0 1.218, d_4^{21} 1.193, n_D^{20} 1.514, RM_D 24.22 (calcd. 24.07); II $\text{HS}(\text{CH}_2)_n\text{CH}_2\text{S}(\text{CH}_2)_m\text{CH}_2\text{Cl}$, b_{20} 120–7°; III $\text{S}(\text{CH}_2)_n(\text{CH}_2)_m\text{S}$, m. 111° subliming above 127°; I is transformed by I_2 into $\text{S}_2(\text{CH}_2)_n(\text{CH}_2)_m\text{I}_2$ (cf. Bennett, *C. A.* 15, 2061; 17, 61) and in turn by HNO_3 into $\text{Cl}(\text{CH}_2)_n\text{CH}_2\text{SO}_3\text{H}$. With acetone, I yields $\text{Me}_2\text{C}(\text{S}(\text{CH}_2)_n\text{CH}_2\text{Cl})_2$, b_{20} 52–60° (decompn.) $d > 1$, miscible with alc., Et_2O and PhH , which on oxidation yielded $\text{Me}_2\text{C}(\text{SO}_3\text{CH}_2\text{CH}_2\text{Cl})_2$, m. 68–9°. With $\text{HBr} \cdot 5\text{H}_2\text{O}$, $\text{CH}_2\text{CH}_2\text{S}$ yielded $\text{Br}(\text{CH}_2)_n\text{CH}_2\text{SH}$, b_{13} 50–1. Similarly with HCl the butylene

sulfide gave a product, $\text{C}_4\text{H}_8\text{ClSH}$, b_{20} about 61°, d 1.07.

The synthesis of benzoyletaurine. R. L. BROWN. *C. L. A. SCHMIDT AND W. E. SCOTT. Proc. Soc. Exptl. Biol. Med.* 19, 403–3(1922).— BzOH and taurine were simultaneously fed to both man and dogs. In the urine about 60% of the taurine was recovered; hippuric acid was present but no estimable amt. of benzoyletaurine. Benzoyletaurine was synthesized by shaking 5 g. of taurine with 10 g. of BzCl in the presence of sufficient NaHCO_3 to keep the reaction slightly alk. Benzoylation was continued until no N_2 was obtained when a portion was treated with HNO_3 . The soln. was then slightly acidified with HCl , cooled, filtered, evapd. to dryness at a low temp. and extd. with petroleum ether to remove BzOH . Benzoyletaurine was then dissolved from the residue by dry AcOEt . Purification is difficult. C. V. B.

A new class of complex compounds of ruthenium. A. GUTBIER. *Ber.* 56B, 1008–11(1923); cf. *C. A.* 16, 691.—If, in the prepn. of the alkylammonium halide complexes of Ru^{IV} , halides 4 mols. of the org. component are used instead of the usual excess of the Ru halide and the reaction is carried out in the presence of enough of the halogen acid, instead of the compds $\text{RuX}_4 \cdot 2\text{RNH}_2\text{X}$ there are formed compds. of the type

$RuX_4 \cdot 4RNH_2X$. Those of the Cl series are purple to brown-red, those of the Br series mostly black, being dark red in only a few cases. In pure H_2O they dissolve apparently without change at first but the solns. quickly darken and soon become an opaque black; abs. alc. dissolves them too little to serve as a medium for recrystn.; aq. ales. decomp. them as easily as H_2O ; aq. and alc. halogen acids, however, dissolve them without decompn. These solns. react instantly with Cl or Br at room temp. with deposition of the hexahalogen salts. In the absence of convincing evidence to the contrary, G. adopts with Weinland for the constitution of these compds. the views of Werner that they are *dihalogenetralkylammonium halide-ruthenic halides*, $[X_2Ru(XH_2NR)_4]X$. The salts of both the Cl and Br series of the following amines were prepd.: methyl-, ethyl-, propyl-, isopropyl-, butyl- and isobutylamines, ethylene- and propylenediamines, pyridine and quinoline. C. A. R.

Constitution of natural muscarine. S. SCILBA. *Atti accad. Lincei* (v), 31, ii, 518-20(1922).—In order to ascertain if muscarine has the aldehydic structure usually assigned to it, S. treated with the Angeli-Rimini aldehyde reagent an ext. prepd. from *Agaricus muscarius*; no hydroxamic acid was, however, obtained, although the ext. showed distinctly the physiol. effect of muscarine. To obtain a definite decision on this question, the prepn. of a larger quantity of muscarine is contemplated. J. C. S.

Correlation of additive reactions with tautomeric change. I. The aldol reaction. EDITH H. USHERWOOD. *J. Chem. Soc.* 123, 1717-26(1923).—This series of studies was undertaken to ascertain whether the reversibility of typical additive reactions is an absolutely general phenomenon and to det. the effect of temp. and structure of the substances involved upon the equilibria. The fundamental point of view adopted is: Every mobile triad system $[11]-X-Y=Z$ may be regarded as consisting of 2 elementary parts, $[11]-X$ and $Y=Z$, by the interunion of which tautomeric change takes place; since this tendency towards the interaction of the 2 residues operates no matter whether they are in the same or in different mols., each tautomeric change will be found to have its counterpart in a reversible process depending on the sepn. of mobile H. In general the existence of equilibria in aldol reactions has escaped notice because the simple additive process is usually only the 1st stage of a more or less complex series of reactions. $Me_2CHCH(OH)CMe_2CHO$ (I) is the simplest aldol which precludes the possibility of further reaction. When I is treated with aq. K_2CO_3 under conditions similar to those used in its prepn. considerable quantities of Me_2CHCHO are produced. At 60° the true equil. is close to 66.8% I and 33.2 Me_2CHCHO , this value being reached in about 10 hrs., starting from either product. Diln. favors the fission reaction. An increase in temp. causes a marked shift in the equil. in favor of the aldehyde. I, on heating at atm. pressure, decompn. quant. into Me_2CHCHO . The aldehyde in Et_2O may be approx. quant. detd. by its reaction with NH_3 , forming the compd. $C_8H_{16}ON_2$. C. J. WEST

Metallic hydroxy acid complexes. I. Cuprilactates. IAN WM. WARK. *J. Chem. Soc.* 123, 1815-26(1923).—The compds. formed between the higher ales., the sugars and HO acids and certain acidic oxides on the 1 hand and certain basic oxides on the other, are of the same structural type and the alc. HO group may function either as a base or as an acid in their formation. The metallic complexes are the more stable, the more strongly the alc. HO group functions as an acid. This leads to an explanation of why only the α -HO acids in the aliphatic series and the *o*-phenolic acids in the aromatic series form such complexes. When NaOH is added to a soln. of Cu lactate, the soln. remains neutral but deepens in color until the ratio of NaOH (mols.) to Cu (atoms) is 1, when $Cu(OH)_2$ begins to sep. Much Cu remains in soln. when the ratio $2NaOH:Cu$ is reached. About this point the soln. becomes alk. to litmus and phenolphthalein and if heated all the Cu is pptd. as CuO . If still more alkali is added, the liquid becomes strongly alk., there is an intensification of color and it can then oxidize glucose. The formation of a Na cuprilactate, $[Cu(O_2H_4C_2)_2]Na_2$, is assumed. Attempts to isolate the Na, NH_4 , K and Ba salts proved unsuccessful and none of the heavy metal salts is sufficiently insol. in H_2O to be pptd. by double decompn. The Na salt is stable only in the presence of a large excess of Na lactate. These salts are incapable of oxidizing glucose; H_2S ppts. CuS from their solns. The Cu-ion concn. is of the order of 10^{-3} . II. Cuprimalates. Their formation, properties and composition. *Ibid* 1826-40.—The system $Cu(OH)_2$ -malic acid- H_2O has been partly investigated at 15° and 50°; qual. diagrams are given which show why it is that, at the ordinary temp., neither the normal nor the acid Cu^{II} malate can be purified by recrystn. 3 salts were isolated: Liebig's salt, $Cu(CuC_2H_3O_6)_2 \cdot 5H_2O$, green; acid cupric malate, $Cu(C_2H_3O_6)_2 \cdot 2H_2O$, pale blue plates which retain their water of crystn. at 105°; normal salt, $CuC_2H_3O_6 \cdot 3H_2O$, deep blue needles. During the dehydration of this salt, the color deepens and the product is extremely sol. in H_2O ; this is designated *cuprimalic acid*,

$\text{HCu}_2\text{H}_2\text{O}_4$. *Na salt*, $\text{NaCu}_2\text{H}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$, deep blue, is obtained by dehydration of an aq. soln. with abs. EtOH. *NH₄ salt*, with $4\text{H}_2\text{O}$, bright blue. *Ba salt*, with $7\text{H}_2\text{O}$, pale blue. *Ag salt*, with $2\text{H}_2\text{O}$, pale blue, darkening on exposure to light. *Pb salt*, probably of complex compn. Liebig's salt is the *Cu salt*. A *basic Cu salt*, $\text{Cu}(\text{Cu}_2\text{H}_2\text{O}_4)_2 \cdot \text{CuO} \cdot 5\text{H}_2\text{O}$, is also described. Measurements of mol. wts. in aq. solns. of the acid, the Na and NH_4 salts and of normal Cu malate indicate a partial association in concd. solns. The concn. of the Cu ion in solns. of these compds. has also been measured. The value in solns. of Na and NH_4 salts is of the order 10^{-4} when the total Cu-ion content is 0.05 g.-at. per l. The acid and normal Cu malate yield identical solns. in which the value is 1.5×10^{-3} ; this soln. contains an equil. mixt. of the 2, the normal malate predominating. The constitution of these salts will be considered later. C. J. WEST

The action of thionyl chloride on α -hydroxy acids. E. E. BLAISE AND MONTAGNE. *Compt. rend.* 174, 1553-5 (1922).—The study of the action of SOCl_2 on primary alc. acids (cf. C. A. 16, 2480) is extended to $\text{MeCH}(\text{OH})\text{CO}_2\text{H}$ (I) and to $\text{CMe}_2(\text{OH})\text{CO}_2\text{H}$ (II). The chlorosulfite of the acid chloride was not obtained, but compds. of a new type designated for lack of any previous term, "*anhydrosulfites of alc. acid*." Their formation is probably due to the chlorosulfite of the acid (first formed) losing HCl , thus: $\text{II} \rightarrow \text{Me}_2\text{C}(\text{CO}_2\text{H})\text{OSCl} \rightarrow \text{Me}_2\text{C}(\text{CO}_2\text{O})\text{SO}$. Lactic anhydrosulfite

(III), b_p 72–4°. *Hydroxyisobutyric anhydrosulfite* (IV), b_p 63°. Both decompd. 120–5° at atm. pressure liberating SO_2 and leaving a *polylactide residue*, a white, neutral mass, regenerating on boiling with alkalis the corresponding alc. acid. III and IV were very sensitive to humidity, and III formed, on standing in the air, crystals, m. approx. 90°, which rapidly disappeared, leaving I. The reaction was probably $\text{MeCH}(\text{CO}_2\text{O})\text{SO}$

$\rightarrow \text{MeCH}(\text{OSO}_2\text{H})\text{CO}_2\text{H}$ or $\text{MeCH}(\text{OH})\text{CO}_2\text{SO}_2\text{H} \rightarrow \text{SO}_2 + \text{MeCH}(\text{OH})\text{CO}_2\text{H}$. No intermediate compd. could be detected in the case of IV. Alcs. reacted on anhydrosulfites to give a quant. yield of the ester of the corresponding alc. acid, with liberation of SO_2 . Arylamines transformed them quant. to the amide of the corresponding alc. acid with liberation of SO_2 . α -Hydroxyisobutyric anilide, m. 130–1°. With PhNHNH_2 , the SO group was attacked, thus: $\text{Me}_2\text{C}(\text{OH})\text{CO}_2\text{H}$

+ $\text{PhNHN}:\text{SO}$. SOCl_2 gave with I (besides III) α -chloropropionyllactic chloride, $\text{MeCHClCO}_2\text{CHMeCOCl}$, b_p 100–3°. This was also obtained by the action of MeCHClCOCl on I. Anilide, b. 116.5°. SOCl_2 and II similarly formed α -chloroisobutyryl chloride, b_p 113–4°, anilide, m. 69–79°, and α -chloroisobutyryl- α -hydroxyisobutyryl chloride, b_p 99–101°, anilide, m. 115°. C. C. DAVIS

Resolution of racemic amino acids not occurring in nature. Resolution of polypeptides composed partly of amino acids not occurring in nature. F. ABDERHALDEN AND SUSI GLAUBACH. *Fermentforschung* 6, 348-56 (1922).—*dl*- α -Bromoheptylic acid b_p 145–51°, *dl*- α -aminoheptylic acid (I), decomp. 275°, *dl*-benzoylaminoheptylic acid, m. 124–6°, *chloroacetyl-dl*-aminoheptylic acid, m. 101–4°, *glycyl-dl*-aminoheptylic acid (II), decomp. 218°, *dl*- α -bromoiso-caproyl-*dl*-aminoheptylic acid, m. 98–102°, and *dl*-leucyl-*dl*- α -aminoheptylic acid, decomp. 247°, were prepd. by the usual methods. Living yeast destroys the *d*-form of I. *l*- α -Aminoheptylic acid is more sol. in H_2O than the racemic acid; it decomp. 274°, $[\alpha]_D^{20}$ 4.21. Yeast maceration juice hydrolyzes II.

R. L. STEHLE
The chloropyruvic acids. M. E. KIMENKO. *J. Russ. Phys. Chem. Soc.* 49, 280-83 (1917).—K. confirms the data of a previous paper (*J. Russ. Phys. Chem. Soc.* (2) 34, 41) on the action of Cl on pyruvic acid (I). K. prepd. dichloropyruvic acid, $\text{C}_2\text{H}_2\text{Cl}_2\text{O}_3$ (II), m. 115–6°, from dry Cl and I; with EtOH and dry HCl it gives the Et ester, which differs from the products obtained by Bettinger, Bekurt and Otto by the action of PCl_5 on pyruvic acid. Seissl's mixts. of mono- and dichloropyruvic acid are in reality Et dichloropropionate. GEORGE W. PUCHER

Cleavage of furyl alcohol and mechanism of the formation of levulinic acid from hexoses. RUDOLF POMMERER AND WILHELM GUMP. *Ber.* 56B, 999-1008 (1923).—From 130 g. furyl alc. (I) refluxed 3 hrs. in 0.1% HCl in MeOH , made alk. with powd. K_2CO_3 , filtered and fractionated *in vacuo*, is obtained 74 g. distillate, b_{15-1} 70–109°, which, after purification through the NaHSO_3 compd., yields, under 14 mm., 3.5 g. b. below 85°, 3 g. b. 85–6°, 6.1 g. b. 86–90° and 21 g. b. 90–7°. The 85–6° fraction is practically pure Me levulinatc (II), identified through the phenylhydrazone, m. 103–4°, *p*-nitrophenylhydrazone, m. 136°, and the *semicarbazone*, m. 148–9° and sol. in NaOH with yellow color. The 90–7° fraction is a very difficultly sep. mixt., 30 g. after 4 fractionations yielding 5.4 g. b_p 99–101° and 3.5 g. b_p 102–5°; another sample of this *o*-methoxy-

levulinoldehyde dimethyl acetal, $\text{MeOCH}_2\text{COCH}_2\text{CH}_2\text{CH}(\text{OMe})_2$ (III), was obtained, in probably purer form, from the Me ether of I (see below) and b_{15} 97-8°, d_4^{20} 1.0323, n_D^{20} 1.4295; it is an oil of faint acetal-like odor, miscible with H_2O , petr. ether and other usual solvents and has a mol. reducing power (Bertrand method) of 0.27 (glucose = 1). The Me ether of I, b_{15} 133-5°, was obtained in 50-60% yield with Me_2SO_4 in cold 40% KOH; 50 g. refluxed with 0.1% HCl in MeOH yielded 4.1 g. III. III dissolves in a concd. aq. soln. of equal parts $\text{H}_2\text{NCONHNH}_2\cdot\text{HCl}$ and NaOAc with evolution of heat but the resulting, easily sol. product has not yet been isolated in cryst. form; in hot aq. soln. with an excess of $\text{H}_2\text{NCONHNH}_2\cdot\text{HCl}$ and 1 equiv. of NaOAc there is obtained a dehydrated δ -hydroxylevulinoldehyde disemicarbazone, $\text{H}_2\text{NCONHN}:\text{CHCH}_2\text{CH}_2\text{C}:\text{N}:\text{NH}:\text{CO}:\text{NH}:\text{CH}_2$, pale yellow, m. 222°, sol. in about 1,000 parts hot H_2O , easily

sol. in dil. HCl and org. acids, sol. in NaOH with yellow color. With 3 g. $p\text{-O}_2\text{NC}_6\text{H}_4\text{NHNH}_2$ in cold 50% AcOH III gives 1.5 g. of a p -nitrophenylhydrazone, $\text{C}_{11}\text{H}_{11}\text{O}_7\text{N}_3$, m. 216-7°, mol. wt. in boiling $\text{C}_6\text{H}_5\text{N}$ 554-622, sol. in concd. H_2SO_4 with deep red, in alc. KOH with blue color; if the reaction is carried out in 2% HCl there is obtained on just neutralizing in the cold with soda 1 g. of yellow-brown, rather unstable flocks which could not be recrystd. but whose compn. points to the possibility that there has been formed a pyridazine which has also added H_2O , perhaps in the sense of the formula $\text{HOCH}_2\text{C}:\text{CH}:\text{CH}_2\text{CH}(\text{OH})\text{NH}:\text{NC}_6\text{H}_4\text{NO}_2$. It has not been possible thus far to

isolate the free aldehyde corresponding to III; III is quite stable towards cold dil. mineral acids; on heating, there soon develops a sharp, somewhat astringent odor which may be due to the free aldehyde but steam carried over only little of any substance with aldehydic properties, as boiling mineral acids convert the III chiefly into levulinic acid (IV) (70%, isolated as the semicarbazone, after boiling 0.5 hr. with 0.4 N HCl); likewise, III refluxed 3 hrs. in about 0.5 N HCl in abs. MeOH gives 63% II (as the semicarbazone). It has been shown that in the formation of IV from hexoses with boiling mineral acids α' -hydroxymethylfural (V) is an intermediate product but so far no explanation has been given of the decompn. of the V into HCO_2H and IV. P. and G. believe that the ring in V is first ruptured, with formation of $\text{OHC}(\text{COCH}_2\text{CH}_2\text{COCH}_2\text{OH})$, which then undergoes acid hydrolysis to HCO_2H and $\text{OHCCH}_2\text{CH}_2\text{COCH}_2\text{OH}$ (VI). If the aldehyde group were split off as HCO_2H before the ring is ruptured the primary product should be I and it was found that I boiled with dil. mineral acids gives only 5-40% IV, depending on the conditions, so it is not very probable that the conversion of V into VI follows this course. C. A. R.

The amides of hyporhodanous (hypothiocyannous) acid. HANS LÉCHER, MAX WITTMER AND WALTER SPEER. *Ber.* 56B, 1104-12(1923).—This acid is the hypothetical SCN analog, HOSCN, of HOCl (Bjerrum and Kirschner, *Die Rhodanide des Goldes und das freie Rhodan*, Copenhagen, 1918, p. 11), and it was hoped that its amides, NCSNR₂, the analogs of the chloramines, might be prepd. and that from these the mustard oil NCSN:C:S and NH_2SH might be obtained through the salts, NCSO₂M and NCS₂M (M = metal), of the acid and the hydrosulfide, resp. The desired object was attained by a slight modification of Söderbäck's expts. (C. A. 14, 1808); the NH_3 or amine must not be passed into the (SCN)₂ soln. but the latter must be poured into an excess of NH_3 or the amine, when the reaction $(\text{NCS})_2 + 2\text{NHR}_2 \longrightarrow \text{NCSNR}_2 + \text{NHR}_2\text{HSCN}$ takes place without the formation of colored by-products. Rhodanamine, NCSNH₂, the product from NH_3 , was obtained only in crude form, as an oil smelling like HCHO, by evapp. the Et₂O soln. in a high vacuum at a low temp.: it deflagrates spontaneously slightly above 0°, and below 0° its vapor tension is not sufficient to permit of its distn. even in the highest vacuum, but its properties can well be studied on its relatively stable Et₂O soln. Diethylrhodanamine, obtained in 75-80% yield from the (NCS)₂ from 7.5 g. Pb(SCN)₂ and 1 cc. Br in 50 cc. Et₂O dropped into 5 g. NH_4Et in 25 cc. cold Et₂O, then shaken with ice H_2O and dried with Na_2SO_4 , b_1 37° (cor.). oil of a pleasant odor, lighter than and not miscible with H_2O , stable for about a week in the ice chest when distd. only once; a very pure product, twice distd., is quite unstable. These amines are quickly decompd. by acids. They immediately produce an intense bluing of acidified KI-starch paper. According to the views of B. and K. and of S. as to the mechanism of the decompn. of (NSC)₂ by H_2O (intermediate formation of NCSOH followed by the further reactions $2\text{NCSOH} \longrightarrow \text{NCSH} + \text{NCSO}_2\text{H}$; $\text{NCSOH} + \text{NCSO}_2\text{H} \longrightarrow \text{NCSH} + \text{NCSO}_2\text{H}$; $\text{NCSO}_2\text{H} + \text{H}_2\text{O} \longrightarrow \text{NCH} + \text{H}_2\text{SO}_4$) the acid hydrolysis of the above amines should proceed according to the scheme $3\text{NCSNR}_2 + 4\text{H}_2\text{O} + 3\text{HX} \longrightarrow 2\text{HSCN} + \text{H}_2\text{SO}_4 + \text{HCN} + 3\text{NHR}_2\cdot\text{HX}$. As a matter of fact, the amines do yield these products but the amt. of H_2SO_4 is somewhat, that of HCN

considerably, less than that calcd. for the above scheme, and the same is true in the hydrolysis of $(\text{NCS})_2$ by H_2O ; the further decomn. of a certain part of the NCSOH first formed, therefore, does not proceed according to the above scheme. That the 1st phase of the acid hydrolysis also does not consist exclusively in the formation of $\text{NCSOH} + \text{NHR}_2$, HX is shown by the results of the alk. hydrolysis, in which the main reaction is $\text{NCSNR}_2 + \text{KOH} \rightarrow \text{NCOK} + \text{S} + \text{NHR}_2$; this is also true of $(\text{NCS})_2$, and the 1st phase of the reaction must be $\text{NCSNR}_2 + \text{KOH} \rightarrow \text{NCOK} + \text{NR}_2\text{SH}$, followed either by the successive reaction of several mols. with each other with elimination of NHR_2 according to the scheme $\overline{\text{H}}|\text{S}|\overline{\text{NR}}_2 + \overline{\text{H}}|\text{S}|\overline{\text{NR}}_2 + \overline{\text{H}}|\text{S}|\overline{\text{NR}}_2$, etc., or by further hydrolysis, $\text{HSNR}_2 + \text{H}_2\text{O} \rightarrow \text{HSOH} + \text{NHR}_2$, and condensation of the labile HSOH to mol. S ($8\text{HSOH} \rightarrow \text{S}_8 + 8\text{H}_2\text{O}$). The acid hydrolysis also apparently follows this course to some extent, for there are obtained some CO_2 and an equiv. excess of NH_4 salt, which points to the intermediate formation of NCOH . C. A. R.

The rotatory property of *l*-aspartic acid and of its salts with alkaline metals. M. A. RAKUZIN. *J. Russ. Phys. Chem. Soc.* 49, 1, 245-7 (1917).—As R. has previously shown (*C. A.* 9, 3050) the $[\alpha]_D$ of alkali metal salts of proteins and of NH_4 acids increases with the at. wt. of the cation. This is corroborated in the present expt. The $[\alpha]_D$ values were as follows: *l*-aspartic acid 3.63°; Li salt -4.86°; NH_4 salt -7.60°; Na salt -9.09°; K salt -14.20°. The possibility of an explanation by the operation of Walden's inversion of optical antipodes is mentioned. The change of sign in the rotation of an NH_4 acid under the influence of alkali was first observed by Pasteur and is borne out by R.'s expts. W. A. PERLZWEIG

The rotatory power of arabic acid and of alkali metal arabates. M. A. RAKUZIN. *J. Russ. Phys. Chem. Soc.* 49, 1, 247-50 (1917).—The principle of increasing $[\alpha]$ with the increasing at. wt. of the cations of the metal salts of proteins and NH_4 acids described in the preceding abstr. was found to hold also for salts of arabic acid. The $[\alpha]_D$ values found are: Li arabate -17.81°; NH_4 salt -19.81°; Na salt -21.67°; K salt -23.06°. The revised value for $[\alpha]_D$ -27.86° for pure arabic acid is given. W. A. PERLZWEIG

Barbituric acid. II. WALTER BOCK. *Ber.* 56B, 1222-7 (1923); cf. *C. A.* 17, 982.—Five g. barbituric acid (I) in 60 cc. warm H_2O treated with Cl_2 until 3 g. has been absorbed gives about 5 g. of the 5-Cl acid (II), faintly pink after long drying at 100°, reddens above 200°, darkens at higher temps., m. 290-5° (Biltz and Hamburger, *C. A.* 10, 2717, give 280°); NH_4 salt, can be recrystd. from H_2O , becomes pink on long drying at 100°, changes to red-brown above 200°, m. 245°. 5,5-Dichlorobarbituric acid (III), from I in hot H_2O with 2 mols. Cl_2 , m. 209-11°, has an acid reaction. 5-Bromobarbituric acid, dissolved in just the necessary amt. of warm H_2O , treated with 0.5 vol. fuming HCl and heated a few min. yields II almost quant. II, on the other hand, is practically unchanged by hot H_2O and some is recovered even from HCl after heating 1.5 hrs., but the positive incrustation paper test points to the presence of I and therefore to incipient decomn. 5,5'-Dichlorohydurilic acid (IV) yields II when boiled 15 min. in H_2O . Di- NH_4 salt of IV, $\text{C}_4\text{H}_6\text{O}_4\text{N}_4\text{Cl}_2 \cdot 2.5\text{H}_2\text{O}$, almost colorless, becomes dark red when dehydrated at 120°, darkens 140°, m. about 235°, is difficultly sol. in H_2O but even slight traces of it impart an intense red color to the H_2O ; the color of the soln. disappears on heating, probably owing to decomn. It is believed that the H_2O is H_2O of constitution and that the dehydration may be represented by some such scheme as $\text{HN}_2\text{C}(\text{OH})\text{OM}$ (colorless) \rightarrow $\text{N}:\text{COM}$ (intensely colored) + H_2O . III in cold

satd. soln. with Cl_2 evolves CO_2 and gives a mixt. of $\text{CCl}_3\text{CONHCONH}_2$, m. 148-9°, with some IV. I treated in warm KOH with Br until the soln. strongly bleaches litmus paper evolves CO_2 and gives $\text{CBr}_3\text{CONHCONH}_2$, m. 158-9°; if the addn. of the Br is stopped before the CO_2 evolution (about 8 g. Br for 5 of I), *K* 5-bromobarbiturate seps. on cooling. C. A. R.

The influence of some normal salts on the mutarotation and specific rotation of glucose. HANS MÜRSCHHAUSER. *Biochem. Z.* 136, 66-70 (1923); cf. *C. A.* 16, 2118.—In retarding mutarotation the alkali halides (except NH_4Cl) are more effective than the alkali nitrates (except NH_4NO_3). NH_4Cl , $(\text{NH}_4)_2\text{SO}_4$, MgSO_4 , and the alkali acetates accelerate mutarotation. 2 *N* solns. of BaCl_2 and CaCl_2 accelerate, 4 *N* or 3 *N* solns. retard, mutarotation. The sp. rotation is decreased by the alkali halides (including NH_4). It is increased by the alk.-earth halides (except Mg). MgCl_2 and the alkali acetates do not affect the sp. rotation of glucose in distd. H_2O . G. E. SWEPSON

Physico-chemical investigations of biological reactions. PAUL HIRSCH. III. **Mutarotation of the sugars.** ANNA E. KOSSUTH. *Fermentforschung* 6, 302-39 (1922).—During the course of the mutarotation of glucose and lactose solns. there were observed

slight changes in the refractive indexes of the solns. which were opposite in direction to those which would be expected from Hudson's theory of the phenomenon. The conversion of (HCHO), into HCHO appears to be associated with a hydration process.

R. L. STEHLE

Acetone-sugars. III. Constitution of the diacetone compounds of glucose and fructose. KARL FREUDENBERG AND ARNOLD DOSER. *Ber.* 56B, 1243-7(1923); cf. *C. A.* 17, 984.—Diacetonehydrazinoglucose, the primary hydrazine obtained by boiling with N_2H_4 , the β -toluenesulfonate of diacetoneglucose (I), allowed to stand 12 hrs. in the least possible amt. of HCl (d. 1.19) quant. gives 3- α,β,γ -trihydroxypropylpyrazole (3-glycerylpyrazole) hydrochloride, m. 139° (cor.), $[\alpha]_{D}^{20}$ yellow -5.6° (H_2O), reacts acid to litmus in H_2O , does not reduce Fehling soln., is oxidized quant. by $KMnO_4$ to pyrazole-3-carboxylic acid, m. 215° (cor.). This shows that it is the 3-HO group in I which is free.

C. A. R.

The unsaturated reduction products of the sugars and their transformations. V. 2-Desoxyglucose (glucodesose). II. MAX BERGMANN, HERBERT SCOTTE AND WOLFGANG LESCHINSKY. *Ber.* 56B, 1052-9(1923); cf. *C. A.* 16, 2118.—Tetrazobenzoylglucodesose, prep'd. essentially as described in the earlier paper but starting from the high-rotating α -form of glucodesose (I), m. 148-9° (all m. ps. are cor.), $[\alpha]_{D}^{16}$ 8.86° in $(CHCl_3)_2$, difficultly attacked by aq. alkalis and acids, even when hot, reduces Fehling soln. only after hydrolysis with alc. KOH, dissolves in cold concd. H_2SO_4 without color, addn. of a drop of H_2O producing an intense raspberry color which after a time slowly changes to a dirty black. In AcOH with HBr it gives benzobromoglucodesose, $O.CHB_2.CH_2.CH(OBz).CHCH(OBz).CH_2.OBz$, m. 139°, $[\alpha]_{D}^{16}$ 121.4° in $(CHCl_3)_2$.

stable only for a short time in the lab. air, converted by Ag_2CO_3 in moist Me_2CO into tribenzoylglucodesose (88% yield), also obtained with Zn dust in 85% AcOH, m. 123°, $[\alpha]_{D}^{19}$ 38.30° in $(CHCl_3)_2$, reduces Fehling soln. but does not give the pine splinter reaction, is relatively stable towards acids but much more sensitive towards alkalis, being quickly decomp'd. by hot dil. NaOH although it dissolves but slightly; the concd. H_2SO_4 soln. gives a raspberry color with H_2O . Tribenzoylmethylglucodesoside, from the Br comp'd. in dry MeOH shaken with excess of Ag_2CO_3 until it no longer gives a ppt. with $AgNO_3$ (yield, 75%), m. 88°, $[\alpha]_{D}^{19}$ -34.31° in $(CHCl_3)_2$, gives a negative pine splinter and a positive H_2SO_4 reaction, has a faint, chalky taste; debenzoylated with NH_3 in MeOH and immediately acetylated by the pyridine method, it gives triacetyl- β ,2-desoxymethylglucoside, m. 96.7°, $[\alpha]_{D}$ -30.3° in $(CHCl_3)_2$. 2-Desoxysorbital (2-desoxymannitol), obtained in 80% yield from I in neutral soln. with Na-Hg, m. 105-6° to a turbid sirup, slowly darkens about 190°, $[\alpha]_{D}^{18}$ 15.61° (H_2O), is more stable towards acids than the aldehydic derivs. described above, does not give the characteristic reactions of desoxy sugars, yields with 0.25% HCl in Me_2CO a diacetone comp'd. $C_{12}H_{22}O_8$ (yield, 70%), b₁ 120-5° (bath temp.), $[\alpha]_{D}^{16}$ 11.08° in $(CHCl_3)_2$, has an intensely bitter and repulsively unpleasant taste. Allowed to stand 24 hrs. with sat'd. Br water, I gives glucodesonic acid, m. 146-7°, $[\alpha]_{D}^{17}$ 4.30° (H_2O) slowly increasing to the const. value 10.85° in about 24 hrs. The acid is isolated as the Ba salt (yield, 26.5%), prisms with H_2O , $[\alpha]_{D}^{19}$ 13.37° (H_2O). In a high vacuum at 100°, the acid slowly loses in wt. and melts, apparently forming the lactone. When 2 g. of the β -form of I, which has a sp. rotation of about 15° in C_6H_5N , is heated 10 min., at first with shaking, with 12 cc. C_6H_5N , cooled, allowed to stand 12 hrs., then treated with petroleum ether to incipient turbidity, the α -form crystals out after several hrs. or days; if crystals of this form are available for seeding it can easily be obtained from a very concd. aq. soln. of the β -form if care be taken to avoid contamination with crystals of the latter form from the lab. air or the clothing of the experimenter. In H_2O neither form shows mutarotation and both have the same rotation, 46.6°, but in C_6H_5N the β -form shows $[\alpha]_{D}$ 15.03° in 5 min. after soln. and 90.21° in 24 hrs. and the α -form 90.11° in 5 min. The course of mutarotation in C_6H_5N is greatly accelerated by the addn. of a little H_2O and still more by MeOH. The so-called α -form is undoubtedly not sterically homogeneous but still contains some of the β -form.

C. A. R.

Constitutional studies in the monocarboxylic acids derived from sugars. I. Tetramethylgalactonolactone and the structure of galactose. JOHN FRYDE. *J. Chem. Soc.* 123, 1808-15(1923).—Galactonic acid, m. 147.5°, $[\alpha]_{D}$ -11.18° (c. 1.1015 in H_2O), after 23 days -37.57° . Methylation of the lactone by Ag_2O -MeI in MeOH and then AcMe gives Me tetramethylgalactonate, b₀₋₇ 100°, n_D^{19} 1.4402, $[\alpha]_{D}$ 9.93° (H_2O , c 1.773). Hydrolysis with $N Ba(OH)_2$ for 1.5 hrs. yields l-tetramethylgalactonolactone, b₁ 130-5°,

n_D^{15} 1.4496, $[\alpha]_D^{15} = -29.51^\circ$ (H_2O , c 1.413) after 6 min., -26.96° after 5 days. Oxidation of tetramethylgalactose with Br gave *d*-tetramethylgalactonolactone, b_p 110-5°, n_D^{16} 1.4571, $[\alpha]_D^{16}$ 106.71° (H_2O , c 1.202) after 9 min. and 16.76° after 1 day. The O bridge in the *l*-form is assumed to be 1:4, that in the *d*-form 1:5. C. J. WGR

Synthesis of glucuronic acid from glucose. MAX BERGMANN AND W. WALTER WOLFF. *Ber.* 56B, 1060-5 (1923).—From 12 g. α -menthol glucoside in 150 cc. C_2H_5N and 12 g. Br in 240 cc. of *N* NaOH allowed to stand 24 hrs., filtered, concd. to 0.5 its vol. *in vacuo*, extd. several hrs. with Et_2O , acidified to Congo with dil. H_2SO_4 and exhaustively extd. with Et_2O is obtained 0.9 g. α -mentholglucuronic acid, microprism with 0.5 H_2O , $m.$ 130°, foam about 10° higher, $[\alpha]_D^{18}$ 51.9° (abs. alc.), reduce Fehling soln. only after hydrolysis with acid; *Na, Ag, Ba, Cd, Pb salts*. For the prepn. of the following derivs. of glucuronic acid (I), the latter need not be isolated; the soln. obtained by heating β -mentholglucuronic acid (II) 2.5-3.0 hrs. with 10 parts of 0.5 *N* HCl was used. From 2 g. II, 1.6 g. NaOAc, 3 g. Ph(PhCH₂)₂NNH₂ and 10 cc. Et_2O (*C. A.* 15, 3624) is obtained 0.8 g. of the lactone benzylphenylhydrazone, $C_{13}H_{14}O_2N_2$, $m.$ 155°, decomp. 158° (Giemsa, *Ber.* 33, 2996 (1900)), gives 141°, $[\alpha]_D^{16} = -25.75^\circ$ (MeOH), sol. in alkalis with salt formation, gives with NH_3 in MeOH the amide, $m.$ 176°. Phenylhydrazide phenylhydrazone of I, $C_{13}H_{12}O_2N_4$ (0.85 g. from 2 g. II, 1.8 g. NaOAc, 3 g. PhNHNH₂ and 8 cc. AcOEt), $m.$ 182°, decomp. 185°. From 2 g. II with 1.6 g. NaOAc and 3 g. PhNH₂ is obtained 0.75 g. of a compd. $(C_{13}H_{14}O_2NNa)_2 \cdot H_2O$, $m.$ 212°, which on soln. in 2.5 cc. H_2O and pptn. with 10 cc. alc. loses 0.5 of the PhNH₂ and gives 0.5 g. of a compd. $C_{13}H_{14}O_2NNa_2 \cdot H_2O$, $m.$ 147° (decompn.). Similarly, 1 g. of the undecompd. II in 2 cc. warm AcOEt with 0.25 g. PhNH₂ gives 0.9 g. of a compd. $C_{13}H_{14}O_2N$, $m.$ 182°, which in freezing PhOH dissociates into its 3 components (2 mols. II and 1 mol. PhNH₂), the mol. wt. found being 231.34. From 60 g. crystd. Ba(OH)₂ in 360 cc. H_2O shaken overnight with 21 g. Br, then 1-2 days with α -Me glucoside is obtained considerable glyoxylic acid, isolated as the benzylphenylhydrazone (4.6 g.), $m.$ 172°, mol. wt. in PhOH 254.3, the free CO₂H group titrating sharply with alkali; methylphenylhydrazone, $m.$ 170°. The acid shows an especially intense naphthoresorcinol reaction, which is therefore not characteristic for aldehydic acids from the 6-C atom sugars. C. A. R.

Structure of cane sugar. MAX BERGMANN. *Ber.* 56B, 1227 (1923).—In connection with the paper of Haworth (*C. A.* 17, 1628), B. points out that he and Mückeley, as the result of their work with the methylcycloacetal of δ -acetobutyl alc., had already explicitly expressed doubts as to the correctness of the then prevailing view of the ethylene oxide structure of cane sugar (*C. A.* 16, 3874). C. A. R.

Two new derivatives of trehalose and mannitol and an α -methyl glucoside dichlorohydrin. BURCKHARDT HELFERICH, ALBRECHT LÖWA, WALDEMAR NIPPE AND HANS RIEDEL. *Ber.* 46B, 1083-7 (1923); cf. *C. A.* 15, 3462.—Trehalose and mannitol undergo with C_2H_5N and SO_2Cl_2 a reaction similar to that of glucosides described in the earlier paper, 4 of the HO groups being replaced by Cl and the remaining HO groups esterified to H_2SO_4 residues, with formation of cryst. compds. A whole series of sugars and sugar derivs. without a free aldehyde group were similarly treated but thus far no other cryst. product has been obtained; apparently, the configuration present in α -Me glucoside is essential for their formation. Mannitol tetrachlorohydrin sulfate, $C_6H_7Cl_4SO_4$ (0.18 g. from 4.4 g. SO_2Cl_2 in 26 cc. C_2H_5N and 50 cc. $CHCl_3$ allowed to stand 2 hrs. in ice with 1 g. mannitol suspended in 7 cc. $CHCl_3$), $m.$ 107°, $[\alpha]_D^{20}$ 105.13° in $(CHCl_3)_2$. Trehalose tetrachlorohydrin disulfate (0.97 g. from 1.7 g. trehalose and 5.8 g. SO_2Cl_2), carbonizes about 175°, $[\alpha]_D^{20}$ 152.20° ($CHCl_3$). α -Me glucoside dichlorohydrin sulfate (I), $m.$ 106°, is now obtained in 36% yield from 10 g. Me glucoside in 220 cc. $CHCl_3$ and 66 cc. C_2H_5N at 15° allowed to stand 2 hrs. with 28 g. SO_2Cl_2 . It splits off no Cl with aq. $AgNO_3$ on the H_2O bath after 15 min. but when shaken with Ba(OH)₂ at 37° it gradually dissolves, using up exactly 1.5 mols. Ba(OH)₂ in about 20 hrs., longer action resulting in no further consumption of Ba(OH)₂. The soln. contains Cl but no SO_4 ions and yields an amorphous chlorinated Ba glucosidosulfate, $C_{12}H_{21}O_{11}Cl_2S_2Ba$. Kept 20 hrs. at room temp. in 60 cc. of alc. which has been satd. at 0° with NH_3 , then evapd. *in vacuo*, taken up in 1 mol. *N* NaOH and evapd. in a high vacuum, 5 g. I gives 2.7 g. of a cryst. *Na salt*, $C_{12}H_{21}O_{11}Cl_2SNa$, reduces Fehling soln. only after heating with dil. mineral acids; *Ba salt*, amorphous; *Cu salt*, $(C_{12}H_{21}O_{11}Cl_2S)_2 \cdot Cu \cdot 3.5H_2O$, blue leaflets, $[\alpha]_D^{16}$ in H_2O 123.87° 4 days after its prepn., 125.56°, 2 days later, $m.$ 125° when freshly prepd., decomp. on standing, reduces Fehling soln. after boiling with dil. mineral acids. The Na salt (1 g.), refluxed 40 hrs. with aq. $CuSO_4$, yields 0.2 g. α -Me glucoside di-

chlorohydrin, m. 155°, $[\alpha]_D^{20}$ 180.7° (alc.), sublimes to a considerable extent at 100° under 0.2 mm., reduces Fehling soln. only after heating with dil. mineral acids; it is also formed slowly by the decompn. of the above Cu salt in the solid form, somewhat more rapidly in H₂O or AcOEt. C. A. R.

The nature of cellosiobiose. GABRIEL BERTRAND AND S. BENOIST. *Compt. rend.* 177, 85-7(1923).—From a study of its rotatory power, reducing action and m. p. B. and B. conclude that the cellosiobiose of Ost and Prosiegel and Ost and Knoth is identical with a no. of intermediate fractions they obtained in their discovery of procloose. These fractions contained cellose and some trisaccharide. R. CHESTER ROBERTS

Constitution of spruce-wood lignin. P. KLASON. *Tidsskrift for Kemi og Bergvaesen* 2, 53-6, 69-72(1922); cf. *C. A.* 17, 1230.—K. finally admits the possibility of a variation of his latest proposed lignin formula (*C. A.* 16, 2487) whereby a CH₂ group should not be situated in the flavone nucleus but between this and the coniferyl nucleus. He gives this variation some advantage, especially if one might suppose that lignin is formed spontaneously by polymerization of coniferyl aldehyde, which should also explain the optical inactivity of lignin. K. will try to show by further investigations that lignin is actually formed in this way. CHR. H. A. SYVERTSEN

Lignin. J. GRÜSS. *Ber. botan. Ges.* 41, 48-52(1923).—The lignin was prepd. by extn. of wood-pulp paper fiber with 4% NaOH and with water. A better yield was obtained from beechwood chips which, however, require a further extn. with alc. and ether. The purified material, after hydrolysis with alc. HCl, gave a substance, C₂₇H₄₀O₁₀, a yellow-white powder, sol. in alc., CHCl₃, and acetone, insol. in ether, benzene, xylene, and water, m. 160°. It appears to be a lignin ester or alc. comparable with coniferyl alc. It dissolves in alkalis with a yellow-brown color, gives a brown-violet color with concd. H₂SO₄ and a red one with phloroglucinol and HCl in alc. Crystals gradually form upon boiling the alk. soln. and the ppt. obtained by acidifying the mother liquor with AcOH no longer gives the red phloroglucinol reaction. The lignin alc. was split and the benzene nucleus went into the cryst. ppt. This ppt. colors red-violet with I₂ and concd. H₂SO₄, changing into a viscous mass. The ppt. decolorizes slightly and becomes cryst. upon refluxing with 1.5% H₂SO₄ but does not saccharify; it no longer dissolves in alkali nor colors with I₂ and H₂SO₄. This property and the failure of the characteristic coloring with resorcinol and HCl show that in lignin alc. the cellulose residue is combined with the benzene nucleus. The color reactions with a no. of alcs. and the effect of various dyes are given. The test given for the detection of lignification is soln. of a mg. of the pptd. lignin alc. in abs. alc. and twice the quantity of pyrocatechol, acidification with HCl and stratification over concd. H₂SO₄. The interphase is colored brown-violet shading into amethyst-violet. Coniferin gives a violet-orange, vanillin a rose-red. The colors are similar but quite distinguishable. Lignin was found by this test in newspaper and in coals. The conclusion is drawn that oxidation processes play only a subordinate role in carbonization. A vanadyl lignin salt, (C₂₇H₄₀O₁₀)V₂ was made which dissolves and crystals from RbOH soln. Digestion of the lignin for 2-3 days with warm perhydrol gave a lignic acid which forms a blue-green salt with CuO. ARTHUR LOCKE

The oxidation of lignin alcohol to lignic acid and the occurrence of the lignic acids in nature. J. GRÜSS. *Ber. botan. Ges.* 41, 53-8(1923).—The lignic acid was prepd. as in the preceding abstr. by warming a lignin alc. prepn. at 60-70° with perhydrol. A yellow soln. was obtained which was dild. with water and treated first with CuO and then with Cu₂O to decomp. the excess of H₂O₂. The green soln. obtained in this way was dialyzed and recrystd. several times. The crystal forms are given, with measurements and plates, in great detail. These data enabled the crystallographic detection of the easily sol. α -lignic acid in rotting oak and pine wood. G. concludes that wood-fungi split out the lignin substance and oxidize it to lignic acid. The lignic acids give an amethyst color going over into a yellow by the pyrocatechol test given in the preceding abstr. The intensity of the color is less than that given by the original lignin material. Lignic acid was found in coals and an acid, mycolignic acid, similar to the β -acid but with a different soly., was found in decayed pine stumps. Further oxidation with H₂O₂ gives hydroxymycolignic acid. The easily sol. Cu lignate is C₂₇H₄₀O₁₀Cu.5H₂O. ARTHUR LOCKE

Analytical investigation of the chemical composition of α -ligninsulfonic acid. P. KLASON. *Svensk Pappers Tid.* 25, 364-6, 385-8(1922).—The Ca salt of α -ligninsulfonic acid (I) was pptd. from sulfite waste liquor with CaCl₂, dissolved and repptd. with CaCl₂. The amt. obtained was 98.5% of the calcd. amt., showing that the CaCl₂ ppts. only the Ca salt. The ratio of C:S = 20. β -Naphthylamine salt (II): β -C₁₀H₇NH₂.HCl, added to the original waste liquor, to solns. of 3 successive pptns. with NaCl, and to

the mother liquor. gave yellow ppts., which, dried, first in air, and then to constant wt. at 120°, had the av. compn. C 63.97, H 5.39, S 5.73, N 2.22; calcd. for $C_{10}H_8SN$, 63.92, 5.19, 5.69 and 2.48%, resp. The ash, 0.45%, contained SiO_2 , and Fe oxides and sulfate. The Cl content corresponds to 0.25% of $C_{10}H_8NH_2HCl$. When the soln. in which the salt is pptd. is heated, the salt m. below 100° to a thick floating mass which cools to a resin and is partly colloidal; after drying it is insol. but when moist and freshly pptd. it is sol. in MeOH, from which soln. it crystals. The waste liquor on standing deposits $CaSO_4$. After standing 2 yrs. the S content dropped from 5.69 to 5.3%. The yellow ppt. formed by the addn. of p -MeC₆H₄NH₂HCl to old waste liquor gave C 62.07, H 5.71, S 5.17, and N 2.12%; calcd. 61.45, 5.54, 6.07 and 2.07, resp. This gives 0.84 atom of S for 20 atoms of C, a value distinctly higher than that obtained by Melander. The α -naphthylamine salt of I, $C_{20}H_{14}O_2SN$, is a yellowish white ppt. which soon becomes granular, and has the same soly. as the β -salt. The phenylhydrazine salt has not been obtained sufficiently pure to det. whether it is a cyclic or a normal salt. The β -naphthylamine salt of methylated I, $C_{21}H_{14}O_2SN$, is, like the non-methylated salt, a cyclic salt and similar to it in appearance. Only 1 Me group can be inserted. The β -naphthylamine salt of α -lignin-oximesulfonic acid, $C_{60}H_{32}O_2S_2N_2 \cdot 6H_2O$, made by adding $NH_2OH \cdot HCl$ and β -C₁₀H₇NH₂HCl to a soln. of a salt of I, white ppt. melting in the liquid at low temp. to a yellowish thick floating mass which cools to a resin; stable in air but loses 8.46% H₂O at 100° and becomes yellow. A condensation product of I with semicarbaside, $C_{61}H_{37}O_{13}S_2N_4 \cdot 5H_2O$, made similarly to the oxime compd., has a similar appearance and properties. It does not lose its H₂O of crystn. completely at 100°. The β -naphthylamine salt of ammoniacal I, $C_{20}H_{14}O_2SN_2$, is yellowish brown. The α -naphthylamine salt of α -ligninhydroxysulfonic acid, $C_{60}H_{32}O_3SN_2$, made by oxidation with H₂O₂, is a white cheese-like ppt. which soon turns yellow. Various possible structural formulas for lignin are discussed. K. gives up his earlier flavone type and adopts one with a similar C skeleton but with a hydroaromatic nucleus and an aromatic nucleus with a flavone ring.

W. SEGERLÖM

Ring-chain tautomerism. VI. The mechanism of the keto-cyclol change in the propane series. E. W. LANFAR AND J. F. THORPE. *J. Chem. Soc.* 123, 1683-9 (1923); cf. *C. A.* 17, 2563.—The general hypothesis used in this series of studies assumed that the angle at which 2 of the valencies of a C atom emerged from the nucleus could be profoundly affected and that 2 of the causes leading to the change were the vol. of the groups attached to the other 2 valencies and the inclusion of these 2 other valencies in a ring complex, the internal angle of which can be assumed to be fixed. It has been suggested that the effect produced may be due to other causes, such as the induced polarities of the C atom forming the grouping R₂. To meet this criticism, the compds. in which R₂ represents a cyclopentane complex have been studied, because if the alteration of the tetrahedral angle is the detg. cause of the observed phenomena, the cyclopentane ring, which give rise to a calcd. angle of 109.4°, ought to exert an influence very similar to that of the Me₂ group. The following work shows this and fully substantiates the above hypothesis. *cis*-Cyclopentanespiro-1-hydroxycyclopropane-1,2-dicarboxylic acid

(I), $(CH_2)_4C \begin{matrix} \diagup C(OH)CO_2H \\ | \\ CHCO_2H \end{matrix}$, m. 163°, by hydrolysis of the Br ester (*C. A.* 9, 3059). *Di-*

Ag salt. Anhydride, m. 71°, from the acid and AcCl. Dianilide, m. 107°, from the anhydride and PhNH₂ at 190°. The mother liquor from I contains the *cis*- and *trans*-1-MeO deriv. of I, sepd. by transforming the *cis*-acid into its anhydride. *trans*-Acid, m. 175°. *Di-Ag salt.* *cis*-Acid, m. 160°. *Di-Ag salt.* The action of boiling HBr on I or its MeO deriv. gives α -ketocyclopentane-1,1-diacetic acid, $(CH_2)_4C(COCO_2H)_2$, m. 112°, also obtained by the hydrolysis of the Br ester with aq. KOH. *Quinoxaline deriv.*, m. 222°. *Di-Ag salt.*

C. J. WRST

Correction (graphite conception of aromatic carbon). A. L. v. STRIGER. *Ber.* 56B, 998 (1923); cf. Kropffleifer, *C. A.* 17, 1228.—Owing to an error in calcn., the value M_{25}^{20} 59.65 for the mol. refraction of anthracene in $C_{10}H_8$ given in v. S.'s paper (*C. A.* 17, 380) should read 65.46; the corrected value agrees well with those found by K.

C. A. R.

Hydrochlorides of the *p*-aminoazo compounds. D. VORLÄNDER AND ERNST WOLFFERS. *Ber.* 56B, 1229-39 (1923).—Some yrs. ago (cf. *Chem.-Zig.* 1907, 922, and earlier papers) attempts were made to show that the color changes in aminoazo compds. produced by acids are due to a process of mol. addn. and not to "salt formation." The present investigation was undertaken to detect by nitrosation or acylation the NH group which is presumably present in the HCl salt of p -Me₂N₂C₆H₄N:NPh (I) if it has the quinonoid structure PhNHN:C₆H₄:NMe₂Cl, and in this connection it was found that the salt

obtained from I in AcCl or BzCl is different from the ordinary salt crystd. from aq. HCl. As a matter of fact, I forms a whole series of addn. products with HCl; the following have been isolated: (1) Anhyd. mono-HCl salt, from abs. Et₂O and 1 equiv. HCl, dark red-violet, m. 168-74° (usually without gas evolution), perhaps identical with the dark, black to red-brown crystals, m. 162-7°, effervesce 173°, prepd. by passing dry air over the hydrated salt or the di-HCl salt at 60-90°; (2) anhyd. di-HCl salt, light red or red, m. about 162°, effervesces around 173°, from the anhyd. mono-HCl salt or that contg. CHCl₃ or C₆H₆ with dry HCl at room temp., perhaps identical with the violet salt from powdered I and HCl gas; (3) mixts. of (1) and (2), or a 1.5 HCl salt, red, m. about 172°, from abs. Et₂O satd. with HCl or from petroleum ether; (4) anhyd. poly-HCl salts, brownish yellow, obtained at low temps. (-60° to -75°) with dry HCl; (5) hydrated salts: (a) mono-HCl salt + 1H₂O, purple with blue-violet surface luster, m. 95-105°, effervesces about 115°, from dil. HCl; (b) dark red leaflets with blue surface luster (apparently a di-HCl salt with more H₂O than (a)), m. about 60°, decomps. about 90°, from HCl of d. 1:1; (6) mono-HCl salt with 1 C₆H₆, gleaming red leaflets, lose their luster above 100° with evolution of the C₆H₆, m. about 165° (decompn.), from C₆H₆ + HCl; (7) mono-HCl salt + 1 CHCl₃, brilliant red needles with blue-violet surface luster, lose their CHCl₃ above 90-100°, m. around 166°, decomp., usually with effervescence, about 175°. The m. and decompn. ps. vary greatly with the previous history of the preps. and with the rate of heating. From CCl₄ with HCl gas is immediately obtained a light red cryst. powder, m. about 148°, with 18.7% HCl; in AcOH HCl produces no ppt.; in AcOEt and CS₂ it gives light red ppts.; in alc., all the salts are sol., usually with dissociation. Unlike that of I, the HCl salt of *p*-H₂NC₆H₄N:NPh adds no solvent when pptd. under the above conditions from C₆H₆, CHCl₃ or Et₂O. *p*-Dimethylamino-*p*'-methoxyazobenzene (II), obtained in 50-60% yield from diazotized *p*-anisidine coupled in AcOH with PhNMe₂, orange, m. 161-3°; moistened with a little alc. and then HCl of d. 1.1 it forms a blue-red soln. of the mono-HCl salt changed by fuming HCl to the red-yellow of the di-HCl salt and back again to blue-red on diln. with H₂O; *mono-HCl salt*, from CHCl₃ with HCl gas, blue cryst. ppt. with metallic luster, becoming brown-yellow when dried over soda-lime *in vacuo* and blue again in moist air, partly dissolves in a little H₂O with violet color, free II remaining behind; *di-HCl salt*, obtained with excess of HCl, is yellow-red; from dry CCl₄ with excess of HCl at -10° to -15° is obtained a brick-red ppt. with 26% HCl. Apparently closely related to II is the *ethoxy homolog*, orange, m. 151°. (*p*-Me₂C₆H₄N₂)₂ (III), obtained in about 8.5 g. yield from 20 g. *p*-H₂NC₆H₄NMe₂, HCl diazotized in 9 g. HCl and 80 cc. H₂O with about 8 g. NaNO₂, at -5° to 0° and added dropwise to a soln., at 15-20°, prepd. from 30 g. crystd. CuSO₄, 13 g. NH₄OH.HCl, 11 g. KOH in 250 cc. H₂O and 100 cc. concd. NH₄OH, yellow-red, m. 273°, gives in CHCl₃ with dry HCl a blue *mono-HCl salt* with blue-green surface luster, becomes light red 90-100°, m. about 220°, partly decompd. by H₂O into the free III; further treatment of the CHCl₃ soln. with HCl gives a red *di-HCl salt*, m. about 190°, becomes superficially violet-black in moist air or after 1-2 days in the desiccator and then contains only 16.8% HCl, dissolves in a little CHCl₃ with violet, in much CHCl₃ with blue color, also in a little H₂O, with loss of HCl; in C₆H₆ and PhMe it is very slightly sol. with yellow-green, in AcOH with green to red-violet, in Me₂CO with green color turning to yellow. All the above facts are against the quinone theory.

C. A. R.

Action of halogens on phenylhydrazones. I. The action of bromine. J. E. HUMPHRIES, EDWARD BLOOM AND ROY EVANS. *J. Chem. Soc.* 123, 1766-72(1923).—In dry CCl₄ at low temp. Br is readily substituted for H of the Ph group attached to the N atom of the phenylhydrazone, the group RR'C:NNH having an *o-p*-directive influence. The nature of the final product depends on the stability of the resulting phenylhydrazone towards hydrolysis by HBr. Most of the products obtained were markedly unstable, particularly in the presence of H₂O, evolving HBr and giving a tarry residue, which yielded the brominated phenylhydrazone or its HBr salt. The results with 13 hydrazones are shown in a table, the color of the ppt., the products and their m. p. and analysis being given. *Acetone-p-bromophenylhydrazone hydrobromide*, pale yellow, m. 155° (decompn.). The main product of the decompn. with H₂O is *p*-BrC₆H₄NHNH₂. *Benzaldehyde 3,4-dibromophenylhydrazone*, pale yellow, m. 127°. *Benzophenone deriv.*, yellow, m. 157°. *m*-Bromobenzaldehyde *2,4-dibromophenylhydrazone*, yellow, m. indefinitely above 150°. PhCH:NNHPh and 2Br₂ or PhCH:NNHC₆H₄Br₂ and Br₂ give the *compd.* PhCBr:NNHC₆H₄Br₂, m. 114°. PhCH:NNHC₆H₄Br₂ and Br₂ give the *compd.* PhCBr:NNHC₆H₄Br₂, m. 113°. Ph₂C:NNH-C₆H₄Br₂ and Ph₂C:NNHC₆H₄Br₂ did not react with Br.

C. J. WEST

Isomerism of the oximes. XII. Hydrochlorides. O. L. BRADY AND F. P. DUNN.

J. Chem. Soc. 123, 1783-1803(1923); cf. *C. A.* 17, 2570.—Continuation of the work reported in *C. A.* 10, 2578. The earlier results must be modified in that only 2HCl salts of PhCH:NOH exist, the one m. 57° having been shown to be a hydrate. Dry HCl passed into benz-*anti*-aldoxime (I) in Et₂O (freezing mixt.) gives the α -HCl salt, m. 105° (decompn.) (the term designates that the *anti*-aldoxime can be regenerated from the HCl). Heated in dry CHCl₃ this yields the β -HCl salt (II), m. 101° (decompn.). In moist CHCl₃ the product formed m. 55°. If the stream of HCl is continued for 1 hr., or if the action takes place in Et₂O without cooling or in boiling CHCl₃ II is formed. Both HCl salts rapidly decomp. in moist air. The hydrated form may also be prepd. by treating I with concd. HCl; this may be dehydrated by allowing it to stand over H₂SO₄ in an atm. of HCl for 1 week. The HCl salt from the *syn*-oxime cannot be converted by soln., etc. into an *anti*-oxime regenerating HCl salt. The α -HCl salt of *p*-methoxybenz-*anti*-aldoxime, m. 134°, results upon passing HCl into the oxime in dry Et₂O. Boiling with CHCl₃ or heating the solid on the H₂O bath converts it into the β -HCl salt, m. 134° and yielding a *syn*-oxime. This salt was also obtained from the *syn*-oxime and HCl in Et₂O, or from the *anti*-oxime and concd. HCl. 3,4-Methylene-dioxybenz-*anti*-aldoxime behaved similarly, the α -HCl salt, m. 170-2°, being converted into the β -HCl salt in boiling C₆H₆. However, the product obtained with concd. HCl is the α -HCl salt, there being no indication of hydrate formation. *m*-Nitrobenz *anti*-aldoxime and HCl in boiling C₆H₆ give the β -HCl salt, m. 135° (decompn.). The α -HCl salt is best prepd. in liquid HCl. 3,4-Dimethoxybenz-*anti*-aldoxime was converted into the *syn*-oxime, m. 110°, by satg. the boiling C₆H₆ soln. with HCl. *o*-Hydroxy-, *o*- and *m*-methoxy-, and 3,5-dibromo-4-hydroxy-benz-*anti*-aldoximes cannot be converted into their *syn*-isomerides by this method. The HCl salt of *m*-MeOC₆H₄CH:NOH on keeping for some years is partly converted into *m*-MeOC₆H₄CONH₂. Technic for this work is indicated, because rapidity of work is essential in order to avoid, as much as possible, decompn. or isomeric change.

C. J. WEST
The properties of benzenecarboxylic acid. WILHELM TREIBS. *Ges. Abh. Kenntnis Kohle* 5, 577-619; *Chem. Zentr.* 1922, III, 1186.—A summary of the properties of numerous acids.

C. C. DAVIS
Aldol condensation between chloral and phenols. II. PAULY and HEINRICH SCHRANZ. *Ber.* 56B, 979-85(1923).—The present work shows that the aldol condensation of aldehydes with phenols is a general reaction; all the mono- and diphenols tried, except *p*-C₆H₄(OH)₂, so reacted with CCl₃CHO.H₂O (I). The products so obtained dissolve at once in cold dil. alkalis and on immediate acidification are reprecipitated unchanged; after acetylation of the phenolic HO group they are no longer sol. in alkalis. At the low temps. used the I usually enters a *p*-position. Anhyd. K₂CO₃ proved to be a reliable condensing agent; although the absence of H₂O is not essential it is in most cases advantageous, as its presence may not only lead to removal of part of the Cl in time but also distinctly increases the tendency to resinification. The amt. of K₂CO₃ need not be more than just enough to produce a distinct bluing of litmus. *p*-Hydroxyphenyltrichloromethylcarbinol, obtained in 60-70% yield from an equimol. mixt. of I and PhOH kept alk. to litmus for 6 weeks with powd. K₂CO₃, m. 87°, is odorless, tastes slightly bitter, has no narcotic but only a phenol action on the organism, gives a NO₂ deriv. with cold, picric acid with hot HNO₃, gives a violet color with FeCl₃, yields with Me₂SO₄ a Me ether which on standing with alkali develops the odor of anisaldehyde, forms with concd. H₂SO₄ a H₂O-insol. chalky ppt.; acetate obtained by boiling a few min. with Ac₂O-NaOAc (under these conditions the carbinol HO group is not acetylated), m. 173°, insol. in cold alkali. The carbinol (2.4 g.) allowed to stand 1 hr. with 1.2 g. PhOH in 2 cc. cold AcOH and 6 cc. H₂SO₄ gives (*p*-HOC₆H₄)₂CHCCl₃, m. 202°. *p*-Cresyltrimethylchloroacetylcarbinol (yield, 50% after 8 weeks), m. 147-8°. 3-Methoxy-4-hydroxyphenyltrichloromethylcarbinol (yield, 72% after 3 months), m. 118-9°, gives a dark indefinite color with FeCl₃; acetate, m. 124°. From the carbinol reduced with Zn dust in 40% alc. on the H₂O bath, filtered, treated with H₂O, extd. with C₆H₆, evapd., acetylated with Ac₂O-NaOAc and oxidized with CrO₃-AcOH is obtained vanillin. With guaiacol in AcOH-H₂SO₄ the carbinol gives diguaiacyltrichloroethane, needles with 1 mol. solvent from CCl₄, m. 98°, also obtained in 222 g. yield from 150 g. guaiacol and 90 g. I in 50 cc. AcOH at 0° treated with 80 cc. concd. H₂SO₄ and allowed to stand 1 day. It also seps. from CHCl₃ in needles with 1 mol. solvent. From 50 g. of the ethane in 150 cc. boiling alc. treated in the course of 12 hrs. with 25 g. Zn dust, then with 50 cc. AcOH and boiled 1 day longer is obtained 3 g. α,β -diguaiacylethylene (dihydroxydimethoxystilbene), m. 200°, shows blue fluorescence both in the solid state and in soln., easily turns pink in the air and begins to smell of vanillin after some weeks; when acetylated, ozonized in CHCl₃ suspension, boiled and sapond., it gives vanillin. 2,3- or 3,4-Di-

hydroxyphenyltrichloromethylcarbinol (obtained in 64-77% yield after 2 months from α - $C_6H_4(OH)_2$), m. 128-9°, gives with $FeCl_3$ the green α - $C_6H_4(OH)_2$, color changed by soda to a dirty wine-red, by NH_4OH to violet. 2,4-Dihydroxyphenyltrichloromethylcarbinol (50% yield from m - $C_6H_4(OH)_2$ after 3 days), m. 176°, gives a deep brown color with $FeCl_3$.

C. A. R.
Tannins and similar compounds. XIII. Stereoisomeric catechols. III. KARL FREUDENBERG AND LUDWIG PURRMANN. Ber. 56B, 1185-94(1923); cf. C. A. 17, 1003.—The Et_2O exts. (more than 500 g.) from 8 kg. Pegu catechu, taken up in 3 l. H_2O and freed from the Et_2O at 50°, left 11 g. quercetin undissolved and from the soln. there crystd. a mixt., ($[\alpha] -5^\circ$ in alc.) of a little *l*-epicatechol (I) with its isomers (*l*-catechol (II), *dl*-catechol (III) and a little *dl*-epicatechol (IV)), which are optically inactive in alc. Recrystn. from 4.5 l. H_2O yielded only the latter alc.-inactive mixt. The combined mother liquors, concd. *in vacuo* to 750 cc., yielded crystals with $[\alpha] -30^\circ$ (alc.). The mother liquors were again concd. and extd. 48 hrs. with Et_2O , which removed a practically alc.-inactive part. The alc.-active part, dried to const. wt. at 90°, was extd. in a Soxhlet with Et_2O until about 0.5 had dissolved. The dissolved part ($[\alpha] -40^\circ$ in alc.) was treated with such an amt. of H_2O at 70° that the fine crystals dissolved and the almost pure, coarsely cryst. I sank to the bottom; after 1 crystn. from H_2O it gave the const. value $[\alpha] -69^\circ$ (alc.). The combined mother liquors were concd. *in vacuo* and allowed to cryst.; all crops with $[\alpha]$ less than -25° (alc.) were recrystd. from H_2O until $[\alpha]$ reached this value and then treated with Et_2O as above. The last aq. mother liquors were always extd. with Et_2O . IV is found chiefly accompanying I; it is recognized by its cryst. form (thick prisms) and removed as soon as it appears in the alc.-inactive fractions. II and III are sepd. by repeated crystn. from H_2O , the course of the sepn. being followed polarimetrically in aq. Me_2CO . I accumulates in the more easily sol. parts until $[\alpha] -10^\circ$ in aq. Me_2CO is reached when, on further crystn., II remains chiefly in the mother liquors. III was recrystd. until completely inactive in both alc. and Me_2CO . Yields: III 320, II 60, IV 30, I 30 g. One sample of Indian catechol on direct crystn. from H_2O gave 50-60% of a white catechol consisting almost entirely of III; another sample, extd. with Et_2O , yielded about 60% of a product consisting of about equal amts. of II and III. From 500 g. of a Gambir catechol, treated in H_2O at 70° with $Pb(OAc)_2$, then with H_2S and concd. *in vacuo* were obtained 85 g. *d*-catechol (V) and 6 g. III. From 100 g. hydrated V heated in 300 cc. H_2O to vigorous boiling in a pressure flask which was then sealed and heated 9.5 hrs. at 125° were obtained 10 g. III, 1.5 g. IV and 2 g. *d*-epicatechol (VI). II after 7 hrs. in H_2O at 108-12° gives considerable I. II seps. with 4 H_2O , m. 93-7° and (anhyd.) 174-5°; $[\alpha] 0^\circ$ in alc., -16.7° in 50% Me_2CO (all values of $[\alpha]$ are for the Hg yellow line); pentaacetate, m. 132°, $[\alpha] -39.4^\circ$ in $(CHCl_3)_2$; tetra-Me deriv., obtained in 60-80% yield from the free II or its penta-Ac deriv. in MeOH with alk. Me_2SO_4 , m. 142-3°, $[\alpha] 12^\circ$ ($\pm 2^\circ$). III, needles with 3 H_2O , m. 214-6° (decompn.); penta-Ac deriv., m. 166°. I, sandy cryst. powder with 4 H_2O , m. 245° (decompn.), $[\alpha] -68^\circ$ (alc.), -60° (50% Me_2CO); penta-Ac deriv., m. 153-4°, $[\alpha] -15^\circ$ in $(CHCl_3)_2$; tetra-Me deriv., m. 153-4°, $[\alpha] -61.5^\circ$ in $(CHCl_3)_2$. VI, m. 245° (decompn.), $[\alpha] 69^\circ$ (96% alc.); pentaacetate, m. 153°, $[\alpha] 16^\circ$; tetra-Me deriv., m. 153°, $[\alpha] 60.9^\circ$ in $(CHCl_3)_2$. IV forms thick plates or, when crystd. above 50°, exceedingly fine needles; the plates have 4 H_2O and m. (anhyd.) 229-32°; pentaacetate, m. 167°. The presence of II or III increases the rotation of I while that of V is apparently not influenced by the epi-forms. F. and P. conclude from their work that the 2 series of catechols are stereoisomers, not structural isomers, with 2 asym. C atoms and that in the rearrangement of an active form the 2 asym. atoms rearrange with perceptibly different velocities so that in the resulting mixt. there are present, besides the original inactive form, 2 racemates and another active form.

C. A. R.
Eseretholmethin and its alcoholate. MAX POLONOVSKI AND MICHEL POLONOVSKI. Compt. rend. 177, 127-9(1923).—Eseretholmethin is a pseudo-base. Its alcoholate prepd. by treating the dry methochloride with $EtONa$ in abs. alc. is an oil, $n_D^{20} 1.14^\circ$, very sol. in water but the soln. on heating gives the cryst. methine, m. 89°.

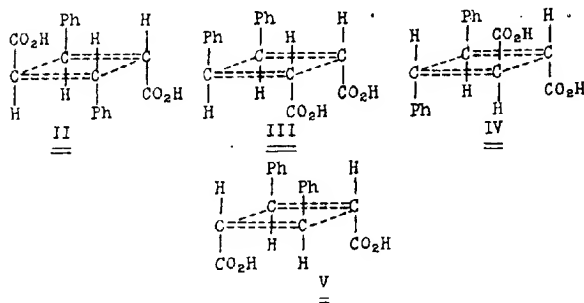
R. CHESTER ROBERTS
Hydrogenation of nitrostyrene. A. GARCÍA BANÚS AND J. PASCUAL VILA. Anales soc. españ. fis. quim. 20, 689-92(1922).—An attempt was made to hydrogenate α -nitrostyrene in an Et_2O -AcOH mixt. at ordinary temp. and pressure with a Pt black catalyst. The desired $Ph(CH_2)_2NO_2$ was not obtained, the products being a mixt. of $PhCH_2CH_2NOH$ and some other unidentified compds.

L. E. GILSON
A method for the bromination of organic compounds. K. W. ROSENMUND AND W. KUHNERN. Ber. 56B, 1262-9(1923).—Both in the satn. of aliphatic double bonds

with Br and in the introduction of Br into aromatic nuclei it is often difficult, by the ordinary bromination methods, to limit the reaction to the desired stage. It has now been found that the Br addn. products of ternary cyclic amines, especially pyridine and quinoline and their salts, serve as well differentiated brominating agents. Thus pyridine dibromide-HBr (I) in AcOH can be successfully used for mild bromination. The Br addn. product of the base need not be preformed; Br can be added to a mixt. of the base (as the HCl salt or acid sulfate) in AcOH and the substance to be brominated. *Safrole dibromide* (α -3,4-methylenedioxyphenyl- β , γ -dibromopropane), bp. 189°, is obtained from 10 g. safrole in 10 cc. AcOH treated at 3-6° with 22 g. I in AcOH suspension; refluxed with AgOAc in AcOH, with subsequent hydrolysis with alc. KOH of the resulting diacetate, it gives the β , γ -di-HO compd., m. 82-3°. *p*-Methoxy- ω -nitrostyrene dibromide is similarly obtained as a brown oil which with alc. KOAc yields *p*-methoxy- ω -bromo- ω -nitrostyrene, m. 67.5-68°. 3,4-Methylenedioxy- ω -nitrostyrene dibromide, stout prisms, becoming superficially yellow in the air with loss of HBr; 3,4-methylenedioxy- ω -bromo- ω -nitrostyrene, yellow, m. 101-2°. Bromopyrogallol, obtained almost quant. from 5 g. C₆H₃(OH)₃ in 15 cc. AcOH with 14.95 g. quinoline dibromide-HBr (II), begins to blacken 120-30° and to decomp. 140°; triacetate, m. 118°. Dibromopyrogallol, from C₆H₃(OH)₃ and the calcd. amt. of I, m. 160° (decompn.); contrary to Eilhorn's statement (*Ber.* 37, 112(1904)), it dissolves very easily in H₂O and immediately afterwards seps. as a voluminous monohydrate, decomp. 137°; triacetate, m. 145°. Dibromoresorcinol, m. 110-2°, gives with FeCl₃ a blue, with CaOCl₂ a violet color soon changing to red and yellow; diacetate, m. 96.5-97°. Bromopyrocatechol, obtained with quinoline acid sulfate, m. 87°, gives with FeCl₃ a blue, with alkali a red color; dibenzoate, m. 111°. C. A. R.

Constitution of the truxillic and truxinic acids and the action of sunlight on the cinnamic acids and the cinnamic acid salts. A. W. K. DE JONG. *Ber.* 56B, 818-32 (1923).—The first part of the paper is a reply to the criticisms of Stoermer (*C. A.* 17, 97) and Stobbe (*C. A.* 17, 549). The sol. neutral salts of *trans*-cinnamic acid (I) were prepd. in the usual way by neutralizing I with the calcd. amt. of the base or its carbonate, the insol. salts by pptn. from solns. of the alkali salts of I with a salt of the base. The di-NH₄ salt (from I in hot alc. with NH₃) loses a large part of its NH₃ on drying in the air, passing over into the acid salt, and could therefore not be used for the illumination expts.; the same was true of the di-Cs and di-Rb salts on account of their hygroscopicity. The Sr, Ba and Pb salts exist in 2 forms, one of which is metastable at room temp. The metastable *Sr* salt, obtained by quickly cooling a boiling concd. soln., seps. in small flat needles soon changing in the soln. into the larger needles of the stable form; in alk. soln. the change is complete in a few hrs. Metastable *Ba* salt, slender 6-sided leaflets slowly changing in faintly acid soln. into very fine, long needles, in neutral or faintly alk. soln. into the thicker needles of the stable form; both forms contain 2H₂O. Metastable *Pb* salt, fine needles; stable form, long needles. *Acid cinnamates*: Li, CsH₂O₂Li.C₆H₄O₂; Rb; Cs; Sr, (C₆H₄O₂)₂Sr.2C₆H₄O₂; Ba. They are obtained by dissolving I in boiling solns. of the neutral salts (satt. at room temp.). No acid Ca salt could be obtained. The acid alk. earth benzoates were also prepd. to det. whether in this case, too, the Ca salt is missing; Ba, (BzO)₂Ba.2BzOH; Sr, and Ca, contain only 1 mol. BzOH per mol. neutral salt, even when an excess of BzOH is used in their prepn. The finely powdered salts were exposed to direct sunlight in very thin layers on glass plates and stirred up daily; at the end of the illumination the acids were liberated with HCl, extd. with Et₂O, freed from I with benzene or by sublimation and sepd. by the method previously described (*C. A.* 13, 3149). To explain the formation of truxillic acids from solid I, de J. proposes a theory based on considerations of the positions of the atoms in the space lattices of the crystals. If mol. compds. are produced by the satt. of secondary valences (Werner) and double bonds possess partial valences (Thiele), then, in the unit cell of the space lattice of I the double bonds of the 2 mols. will be opposite to each other and the 2 mols. will arrange themselves parallel to each other. Bearing this in mind, it can easily be seen that these 2 mols. can arrange themselves in the 4 possible positions II-V and that if they combine in these 4 positions they will form α -truxillic (VI), β -truxinic (VII), ϵ -truxillic (VIII), and δ -truxinic (IX) acid, resp. In crystals, the highest degree of symmetry tends to the greatest stability (Jaeger). Now, II has a center of inversion or symmetry, III a plane of symmetry, IV an axis of the 1st order and is identical with its mirror image and V has likewise an axis of the 1st order but is not identical with its mirror image. Hence, the degree of symmetry, and therefore the stability, of these 4 forms decreases in the order given. These views agree well with the relative stabilities of the known α - and β -I and with the non-existence of the other 2 possible forms of I. For the *cis*-cinnamic acids, 4 possible forms can be derived

in a similar manner but there is no method of proving exptly. that their degrees of symmetry and of stability run parallel, for all 3 of the known forms change in sunlight into β -I. The velocity of polymerization in sunlight of the salts of I varies widely and is always smaller than that of I itself. Thus, after 18 hrs. illumination, 1 g. of substance gave the following amts. of products: I, 0.724 g. VI; neutral Li salt, 0.372 g. VII + 0.01 g. VIII; Na salt, 0.033 g.; K salt, 0.100 g. salt. The Me ester, prepd. from alpenia oil, gave after 8 days only the di-Me ester of VI. Theoretically, the salts of univalent metals would be expected, like I itself, to give 4 forms, of which VI should be the most stable; since VI is not formed the entrance of the metal into the mol. must produce a change in the stability of the possible forms and it can only be concluded that the metal atoms arrange themselves opposite each other; if, as has been shown to be the case for inorg. salts by röntgenographic means, the metal atoms lie in definite planes in rows behind each other and the acid radicals are oriented between these planes in rows, then these salts on illumination can give only VII. VIII is formed always in only very small amt. and as no *cis*-cinnamic acid was found it is very probable that it is produced when the double bond is opened and the C atoms are able for a moment to rotate freely. As



the CO_2Li groups remain next to each other it is only the C atoms bearing the Ph groups which can rotate; if one of these rotates, VIII will result. The salts of the following bivalent metals gave VII and another acid (given below in parentheses, together with the yield, referred to 100 parts VII): Ca (unknown acid, 5.1); metastable Sr (VIII, 10.4); metastable Ba (IX, 27.0); stable Ba (VIII, 42.2); Zn (VIII, 21.0); metastable Pb (IX, 454.0); stable Pb (IX, 75). The unknown acid obtained from the Ca salt m. 214° , depresses the m. p. of α -truxinic acid (m. 209°) to 190° , is quite sol. in hot C_6H_6 , mol. wt. in freezing AcOH 283. The stable Sr and the Cu, Cd, Mn, Fe'' and Co salts gave no truxillic or truxinic acids, the Mg and Ni salts and the Ba salts previously heated to 100° gave only VIII. The acid Sr and Ba salts gave VII, the following acid salts VIII and another acid (given in parentheses, with the yield, referred to 100 parts VIII): Li (IV, 12.3); NH_4 (VI, 21.4); Na (IX, —); K (VIII, 10.5); Cs (IX, 4.6).

C. A. R.

Stereochemistry of the hexahydrotoluidines. A. SKITA. *Ber.* 56B, 1014-23 (1923).—S. and Berendt by catalytic reduction with Pt obtained from each of the toluidines 2 hexahydro derivs. (designated α and β), sep'd. by fractional crystn. of the Bz derivs. (C. A. 14, 1334). The free bases were obtained from these Bz derivs. by sapon. with alkali in sealed tubes, but as the fractional crystn. of the Bz derivs. is time-consuming and wasteful other methods of prepn. were resorted to. Reduction of the acetotoluides (cf. C. A. 14, 3667) with H_2PtCl_6 and colloidal Pt in the presence of sufficient HCl gave exclusively the *cis*-hexahydro derivs. while the *trans*-isomers were obtained quant. in neutral aq. soln., and from these the free bases were easily prep'd. by sapon. Below are the b. p., d_4^{25} , n_D^{20} and $E_{589}^{1\%}$, resp., of these methylcyclohexylamines (Me = 1) and the m. ps. of the Ac, Bz, and phenylurea derivs.: $r^1, 2^\circ$, $153.5-4.0^\circ$, 0.8778, 1.4688, 0.12, m. 82° , 107° , 86° ; $r^1, 2', 150^\circ$, 0.8688, 1.4650, 0.23, 57° , 146° , 130° ; $r^1, 3^\circ$, $152.7-3.4^\circ$, 0.8552, 1.4538, 0.05, 74.5° , 98° , 138.5° ; $r^1, 3', 151.5-2.5^\circ$, 0.8572, 1.4547, 0.04, 63° , 127° , 178° ; $r^1, 3'', 153.3-3.7^\circ$, 0.8567, 1.4559, 0.13, 79° , 116° , 102° ; $r^1, 4^\circ$, $151.5-1.9^\circ$, 0.8543, 1.4550, 0.17, $69.5-70^\circ$, 180° , 176° . The amines are somewhat volatile with Et_2O , eagerly absorb CO_2 from the air (more rapidly in the case of the *trans*-iso-

mers); the *cis*-compds. have a wholly ammoniacal, the *trans*-compds. a coniine-like odor; the cond. const. of the isomers, however, are the same; HNO₃ converts them into the corresponding methylcyclohexanols (C. A. 17, 1787). In confirmation of the view earlier expressed (C. A. 16, 2321) that configurations are to be detd. by the chem. methods of prepn. rather than by the phys. const. of the products, it was found that the const. of the amines prepd. by the catalytic reduction in acid and alk. soln., resp., of the methylcyclohexanone oximes agreed with those of the corresponding amines prepd. in the above 2 other ways. Below are the b. p., d_4^{20} , n_D^{20} and Π_{20}^D of the ketones (prepd. by catalytic reduction of the cresols) and the m. ps. of their semicarbazones and oximes: *1,2*, 166°, 0.9250, 1.4483, 0.12, 191°, 43°; *1,3*, 168°, 0.9136, 1.4430, 0.21, 180°, oil; *1,4*, 170.5°, 0.9138, 1.4439, 0.22, 197°, 36°. Of the above amines, the *cis*-*o*- and *p*-compds. had not previously been described. Contrary to the Anwers rule, the *trans*-*m*-amine shows a higher *d.* and *n.*, as well as a lower mol. refraction, than the *cis*-isomer; to det. whether this anomaly persists in its liquid derivs. the methylcyclohexyl mustard oils were prepd. by the Hofmann method, which gives better yields than v. Braun's thiuram disulfide method; below are the b. p., d_4^{20} , n_D^{20} and Π_{20}^D of the products and the m. ps. of the phenylthioureas: *1',2'*, 228.9°, 0.9680, 1.5338, 0.15, 114°; *1',3'*, 224.5°, 0.9620, 1.5303, 0.18, 144°; *1',3'*, 226.7°, 0.9479, 1.5204, 0.16, 105.6°; *1',3'*, 224.5-5.5°, 0.9487, 1.5206, 0.14, 94-5°; *1',3'*, 227-8°, 0.9470, 1.5208, 0.21, 149°; *1',3'*, 225.5-6.5°, 0.9450, 1.5200, 0.23, 159°. The corresponding const. for the methyl-[methylamino]cyclohexanes and the m. ps. of their picrates are: *1',3'*, 157.5-8.5°, 0.8185, 1.4529, -0.02, 179°; *1',4'*, 154-5°, 0.8440, 1.4512, 0.03, 182°; for the methyl-[dimethylamino]cyclohexanes: *1',4'*, 160-1°, 0.8355, 1.4507, 0.01, 184°; *1',3'*, 156.5-7.0°, 0.8320, 1.4494, 0.04, 184°. The *cis*-methyl[acetylamino]cyclohexanes were obtained in about 12 g. yield from 15 g. of the acetotoluide in 8.5 cc. H₂PtCl₆ (0.85 g. Pt), 80 cc. of 10% aq. gum arabic, 50 cc. AcOH, 10 cc. concd. HCl and 50 cc. colloidal Pt (0.15 g. Pt and 0.9 g. gum arabic) hydrogenated 35 min. at 70-80° under 3 atm. excess pressure; the *o*-compd., b₁ 162-3°, m. 82°; *m*-compd., b₁ 156.5-7.5°, m. 74-5°; *p*-compd., b₁ 160.5°, m. 79°. The *trans*-isomers are obtained in 12.4 g. yield from 15 g. of the acetotoluide in 250 cc. of dialyzed colloidal Pt, contg. 1 g. Pt and 7 g. gum arabic, and 5 cc. alc. hydrogenated 25 min. at 70-80° under 3 atm. excess pressure; the *o*-compd., b₁ 153.5°, m. 57°; *m*-compd., b₁ 159°, m. 63°; *p*-compd., b₁ 156.8°, m. 68-9°. They are hydrolyzed by heating 4 hrs. at 130-40° with concd. HCl. C. A. R.

Derivatives of cyclohexane-1,4-dione-2,3-dicarboxylic acid. BURKHARDT HELFERICH AND H. G. BODENBENDER. *Ber.* 56B, 1112-6(1923); cf. C. A. 15, 2081. By using only 54 g. KCN and a correspondingly smaller amt. of H₂SO₄ (110 cc. of 5 *N* acid at first and then 115 cc. for the acidification) in the prepn. of the dicyanohydroquinol described in the 1st paper, the yield was increased to 70%. The di-Me dimethoxyphthalate was prepd. from the free (HO)₂C₆H₂(CO₂H)₂ with alk. Me₂SO₄ and with boiling alc. KOH gave a good yield of the (MeO)₂C₆H₂(CO₂H)₂ which, unlike Perkin and Weizmann's product (*J. Chem. Soc.* 89, 675(1906)), was colorless; it is easily converted by boiling H₂O into the yellow anhydride, m. 264°. From 1 g. di-Me cyclohexane-1,4-dione-2,3-dicarboxylate (I) in 2 cc. Ac₂O and 0.4 cc. concd. H₂SO₄ poured, after cooling, into about 3 parts H₂O is obtained nearly quant. a diacetate, m. 87.8°, insol. in cold dil. NaOH. In abs. alc. with TIOEt, I gives a *Tl* salt as a thick yellow ppt. sensitive to O, both in the solid form and in soln. and yielding almost quant. the 3-Me deriv. of I on long refluxing with 6 parts MeI. 3-Benzyl deriv. of I (4.5 g. from 5 g. I and 10 g. PhCH₂Br), m. 109° (cor.), gives an intense wine-red color in alc. with FeCl₃, is sol. in alkalis without color and reppd. by CO₂, reduces Fehling soln. in boiling alkalis, NH₃-AgNO₃ on gentle warming; diphenylhydrazone, m. 75-80°. Cyclohexane-1,4-dione-2,3-dinitrile, prepd. from dicyanohydroquinol like I from (HO)₂C₆H₂(CO₂H)₂ (4.2 g. from 10 g. (HO)₂C₆H₂(CN)₂), begins to turn brown 100°, m. 160-70° (decompn.), easily sol. in H₂O and alkalis with lemon-yellow color, is very sensitive to O in alkalis, reduces Fehling soln. and NH₃-AgNO₃ at room temp., gives no color with FeCl₃; di-Na and di-Tl salts; disemicarbazone, turns brown about 200°, does not m. 280°; diphenylhydrazone(?), red-brown amorphous ppt., becomes discolored 180°, m. 226-32°; diacetate, m. 162° (cor.). The dinitrile (1 g.) boiled with 4 cc. concd. H₂SO₄ and 15 cc. H₂O gives 0.5 g. *p*-diketocyclohexane. Di-Me ether of the dinitrile, obtained in 73% yield with CH₂N₂ in Et₂O, m. 202° (cor.), is insol. in KOH, gives no color with FeCl₃, yields *p*-diketocyclohexane with boiling dil. H₂SO₄ but with boiling KOH it gives NH₃, 67% 2,3-dimethylgentisic acid and 23% succinic acid. C. A. R.

Phellandrenes. I. H. G. SMITH, ERIC HURST AND JOHN READ. *J. Chem. Soc.* 123, 1657-70(1923).—Although much work has been carried out by Wallach, Semmler

and others on constitutional problems, little has been done with the object of isolating specimens of high phys. purity and even common methods of diagnosis involve the prepn. and phys. examn. of derivs. which are imperfectly known. The crude oil obtained by steam distn. of leaves and twigs of *Eucalyptus dives* contained about 46% of *l*-piperitone by vol.; the dried oil had d_4^{20} 0.9042 (vac.), n_D^{20} 1.4802, $[\alpha]_D^{20}$ -62.73. 1363 g. oil, by repeated distn., gave 230 g., b_{18} 63-5°, which was then shaken with 140 g. 50% aq. resorcinol for 30 min. to remove the cineole, and again fractionated, giving 50 g. (3.7% of the original oil) of pure *l*- α -phellandrene (I), b_{18} 58-9°, d_4^{20} 0.8410, n_D^{20} 1.4732, $[R_L]$ 45.45, $[\alpha]_D^{20}$ -112°. I is obtained with equal readiness from *E. phellandra*, but there are indications that the associated substances exhibit certain differences in the 2 cases. The α -nitrosite (II) is best prepd. by pouring 25 cc. I in 150 cc. light petroleum into 53 cc. 44% NaNO₂ in a freezing mixt. When the mixt. reaches 0° 25 cc. glacial AcOH is added, the cryst. II removed from the sticky yellow mass by washing with EtOH and recrystd. from AcMe-EtOH. It m. 121-2°. The yield is always less than 5 g. II shows mutarotation: In CHCl₃ $[\alpha]_D^{20}$ changed from 142.6° to -80.1° in 237 hrs.; in C₆H₆, from 234.4° to -103.3°, and in AcMe from 165.9 to -49.3° in 360 hrs. In concd. solns. the mutarotation was more sluggish and less complete than in more dil. solns. During this process the solns. changed in color, and on evapn. of the solvent, an orange-red oil remained, no cryst. material being recovered. Mutarotation was greatly accelerated by warming the solns. At 60° in CHCl₃ there was a rapid decline for the 1st 10 min., then a rise and after 45 min. a gradual decline. The presence of C₆H₁₁N up to a concn. of 0.01 *N* caused no fundamental alteration in the character of the mutarotation but with 0.1 *N* solns. the predominant mutarotation was upward, while in CHCl₃ soln. the initial changes were very similar in general character to those produced by maintaining the soln. at 60° in the absence of C₆H₁₁N. The rotations of specimens of II m. 108-9° to 119-20° are given and emphasize the importance of careful polarimetric control in the diagnosis of phellandrenes by the nitrosite method. C. J. WESS

Conversion of sabinol into thujene. G. G. HENDERSON AND ALEXANDER ROBBYSON. *J. Chem. Soc.* 123, 1713-7(1923).—Reduction of sabinol with H by passing the mixed vapors over pumice-Ni at 170-5° gave thujane, a 2nd satd. hydrocarbon (I), b_{18} 161-3° (Wallach, *C. A.* 14, 3652) and some unchanged sabinol. With H and Pd a mixt. of dihydrosabinol (Wallach), thujane and I was obtained. The phys. consts. of dihydrosabinol prove it to be identical with thujyl alc. The Me xanthate is a dark red viscous liquid which decomp. 160-5° to give thujene (α - and β -isomers). The fractions correspond to those obtained by Kondakov and Skworzow (*J. prakt. Chem.* 67, 573(1903)). C. J. WESS

Reactions differentiating pinene from nopinene. I. Oxidation with permanganate to pinonic and nopinic acids. G. DUPONT AND G. BRUS. *Ann. chim.* 19, 186-98 (1923).—Nopinene could not be detd. in oil of turpentine by oxidation with KMnO₄ because the oxidation was not quant. The nopinic acid was obtained only in the active form. Oxidation of active pinene was accompanied by racemization. A much better yield of inactive pinonic acid was obtained by oxidizing inactive pinene in place of the natural pinene, which is partly active. The yield of pinonic acid was also improved by bubbling CO₂ through the mixt. of KMnO₄ soln. and pinene. T. S. CARSWELL

A new method for the preparation of camphor. PARISELLE. *Compt. rend.* 176, 1901-2(1923).—The 1st step in converting pinene to camphor, the satn. of the former with dry HCl at 20°, usually gives a yield of 60%. By satg. in 2 steps at 2-day intervals this was increased to 75%, and in some cases 85%. The 2nd step, treating the HCl salt with PhONa, gives a 75% yield of a crude camphor contg. considerable phenol, and HCl salt. This is due to the small interval of 22° between the b. p. of camphor and phenol, and to the sepn. of the reaction mixt. into 2 layers. By using com. *m-p*-cresol in place of phenol a yield of 88% camphor is obtained. ROGER G. FRANKLIN

The action of phosphoric acid on rosin, wood tar and a few representatives of the most important classes of substances. MEILACH MELAMID AND EMIL ROSENTHAL. *Z. angew. Chem.* 36, 333-6(1923).—Based on a previous observation that tar from the dry distn. of wood is improved in quality by treatment with H₃PO₄ (cf. Ger. pats. 264,811; 367,013), a study was made of the action of H₃PO₄ when representative substances present in tar oils were distd. with excess H₃PO₄. The action of H₃PO₄ on org. acids was in contrast to the greater activity of H₂SO₄ (cf. *Ber.* 34, 3073; 36, 3558; 38, 839; 39, 51; 40, 4374; 41, 1665; 43, 2503, 2883). *BzOH*, *PhCH₂CO₂H*, *Ph₂CHCO₂H* and *Ph₃CCO₂H*. No CO nor CO₂ was evolved nor any change noted after several hrs.' boiling. *Palmitic acid*. No CO nor CO₂ was evolved. *Et₂CHCO₂H* and *CM₆CO₂H*. CO, unsatd. hydrocarbons (probably β -amylene and isobutylene) and a small amt. of

CO₂ were evolved. *Camphoric acid*. Complete decompn. occurred, and at all stages equal vols. of CO and CO₂ were evolved. The distillate was an oil, C₈H₁₄, b₁₂ 50–70°, and was either CH:CHCM₂CHMcCH₂ or CH₂CH₂CM₂CM₂:CH₂. The reaction was probably C₁₂H₁₆O₄ → C₈H₁₄ + CO₂ + CO + H₂O. *Abietic acid*.—A distillate, yield approx. 65%, was obtained, contg. no O. 68% of the CO₂ possible by calcn. was evolved as a mixt. of CO and CO₂ with a 10% residue. Without H₃PO₄ only 4% distillate was obtained. Hydrocyclic carboxylic acids present in tar probably all form hydrocarbons on distn. with H₃PO₄. *Phenols*.—No decompn. occurred with PhOH or MeC₆H₄OH, but *m*- and *o*-C₆H₄(OH)₂ carbonized and evolved CO and CO₂. *Anthracene and indene*.—No decompn. It is concluded that in mixts. occurring in tar, alics. acids (provided the latter are not primary, aromatic or aliphatic-aromatic) and polyphenols are decompd. but simple phenols and hydrocarbons are not attacked. *Rosin*. The action was similar to abietic acid (because the latter is the chief constituent), the yield after a double rectification being 68.5%, 66% of the possible CO₂ being evolved as CO + CO₂ with a 10% residue. *Wood tar*.—The data show the results for the original tar, after distn. at ordinary pressure, after distn. *in vacuo*, and after distn. over H₃PO₄, resp.: C, 77.33, 74.90, 75.52, 84.53; H, 9.32, 9.09, 8.61, 10.51; O, 13.35, 15.01, 16.87, 5.14; d, 1.003, 0.978, 0.998, 0.960; % yield of oil, —, 17.5, 27.0, 48.5; liberation of O in form of CO₂ and CO + H₂O, —, 2.2, —, 4.6. H₃PO₄ thus improves the yield as well as the quality of the distillate.

C. C. DAVIS

o-Phenylcyclohexanol and the bromohydrin of cyclohexane-1,2-diol. FERRER BEBOS. *Compt. rend.* 177, 111–3(1923).—One of the stereoisomeric forms of *o*-phenylcyclohexanol (I) prepd. by the action of PhMgBr on the oxide of cyclohexane, b₁₁ 138–40°, d₁₅ 1.035, n_D²⁰ 1.5415; its phenylurethan m. 135–6° and its phthalate m. 185–6°. When distd. over KHSO₄ I gives phenylcyclohexane, b₁₁ 125–6°, d₁₅ 0.982, n_D²⁰ 1.5505. A secondary product in this reaction, C₈H₁₆O, b₁ 65°, d₁₅ 1.0, n_D²⁰ 1.499, was obtained and is being studied for future report. The other stereoisomer of I has already been prepd. by the action of Na on *o*-phenylcyclohexanone in abs. alc. and m. 54–5°. The action of H₂O on the intermediate Mg deriv. prepd. while making I was very violent and gave the cyclohexane-1,2-diolbromohydrin, b₉ 87–8°, d₁₁ 1.402, n_D²⁰ 1.528. Its phenylurethan m. 87–8°.

R. CHESTER ROBERTS

Diphenylethylene. J. FERRER. *Anales soc. españ. fis. quim.* 20, 459–66(1922).—Methylfluorenon (I), m. 172–3°, was obtained in good yield from fluorenone and MeMgI. Two g. I mixed with 3 g. AlPO₄ were distd. under 10–2 mm. The product crystd. from petroleum ether and brominated yielded 0.4 g. dibromodiphenylethylene (II), m. 42–3°. II refluxed with EtOH and Zn dust in the light yielded a partly polymerized product but the expt. repeated in the dark-room gave crystals of pure diphenylethylene, (C₆H₅)₂C:CH₂ (III), m. 53°, stable for several hrs. in the dark but completely polymerized and rendered insol. in Et₂O when exposed 10 min. to the light of the Hg arc.

L. E. GILSON

Progressive addition of hydrogen to tetraphenylallene. D. VORLÄNDER AND PAUL WEINSTEIN. *Ber.* 56B, 1122–4(1923).—Ph₂CHC(CH₂)₂Ph₂ (I), m. 127–8°, obtained in 18 g. yield from 20 g. Ph₂C:C:CPh₂ (II) and 1.5 g. red P in 50 cc. AcOH and 4 cc. HI (d. 1.7) rapidly brought to a boil and boiled 4–5 min., is sol. in comcd. H₂SO₄ with yellow color, gives with Br Ph₂CHCBr:CPh₂, m. 124°, which adds no Br in the cold and is reduced back to II by boiling alc. KOH. Boiled 4 hrs. with HI-AcOH I is completely reduced to CH₂(CHPh₂)₂. With excess of CrO₂ in AcOH at 50°, I gives equimol. amts of Ph₂CO and Ph₂CHCO₂H, which agrees best with the formula above for I, although (Ph₂CH)₂C= is not excluded. Supersatd. with Cl in CCl₄ and allowed to stand 4–5 min., then freed from the Cl and solvenc with air, II gives the monochloride, C₆H₄CPh:CClCPh₂, of its cyclic isomer (cf. *Ber.* 39, 1025(1906)), m. 167°, sol. without

color or with faint yellowish color in cold, with dark fuchsia-red color in hot comcd. H₂SO₄, also obtained from II heated with PCl₅. II (2 g.) allowed to stand 3 hrs., protected from moist air, with 5 g. N₂O₂ in 40 cc. C₆H₆ in ice yields 1.2 g. of a nitrosite, C₁₇H₁₆N₂O₂, m. 141–2°, 1 g. of which with alc. SnCl₂ or with HCl gas in alc. or AcOH suspension at 50–60° yields 0.5 g. of the dioxide O.CPh₂.C.CPh₂O, m. 198°, also obtained with CrO₂,

sol. in cold H₂SO₄ with violet, in hot acid with brown color, further oxidized by CrO₂-AcOH to Ph₂CO.

C. A. K.

Action of sodium on diphenylacetic ester. D. VORLÄNDER AND EDGAR RACK. *Ber.* 56B, 1125–29(1923).—To explain the formation of Ph₂C:C:CPh₂ (I) in the dry distn. of (Ph₂CHCO₂)₂Ba, it was assumed that *sym*-tetraphenylacetone (II) is an inter-

mediate product (*Ber.* 39, 1024 (1906)). I has since been prepd. (0.2-0.75 g. from 5 g. molten $\text{Ph}_2\text{CHCO}_2\text{Et}$ on the H_2O bath slowly treated with 3.5 g. Na wire and heated 3-4 hrs., or 10.1 g. from 30 g. $\text{Ph}_2\text{CHCO}_2\text{Et}$ allowed to stand 3-4 days at room temp. in Et_2O with 12 g. Na), but all attempts to convert it into I have thus far failed. II, which is identical with the product obtained by Staudinger from dimerized $\text{Ph}_2\text{C}:\text{CO}$ by cleavage with alkalis (*C. A.* 5, 1767), m. 134° , mol. wt. in boiling C_6H_6 338-69, is not attacked by Na_2CO_3 , NaOH or alc. KOH, forms in H_2SO_4 a colorless soln. becoming yellow on standing or gentle warming, dists. unchanged from P_2O_5 , CaO, BaCO_3 , crystals unchanged from boiling Ac_2O (+ NaOAc), SOCl_2 and POCl_3 , does not react easily with PCl_5 , adds no Br, shows no ketone reactions with $\text{H}_2\text{NCONHNH}_2$, PhNHNH_2 , or NH_2OH ; passed through a 10 cm. tube heated to redness, it yields brown oily and cryst. products from which was isolated some $(\text{CHPh})_2$, m. 207° . Distn. with Zn dust gives CH_2Ph_2 and other products. With CrO_2 in AcOH are obtained Ph_2CO and CO_2 ; with KMnO_4 in Me_2CO , Ph_2CO , some $\text{Ph}_2\text{C}(\text{OH})\text{CO}_2\text{H}$ and a substance m. about 212° , insol. in the usual solvents; with HNO_3 in AcOH, $\text{Ph}_2\text{CHCO}_2\text{H}$. HNO_3 in concd. H_2SO_4 gives a NO_2 deriv. m. around $140-5^\circ$ giving a dark blue-red color with alkalis in Me_2CO . Reducing agents (Zn and AcOH, Na and EtOH or AmOH, boiling HI) attack it practically not at all; fuming HI and red P at $200-10^\circ$ give a little Ph_2CH_2 . Br in CCl_4 in sunlight or arc light gives chiefly a *mono-Br deriv.* (2.1 g. from 3 g. II), m. $78-80^\circ$, evolves HBr when heated with concd. H_2SO_4 , also when heated above its m. p., splits off KBr with hot alc. KOH, forming a cryst. substance which turns reddish in the air and is insol. in dil. acids and alkalis. C. A. R.

Benzal-*asym*-diphenylacetone. EDGAR RACK. *Ber.* 56B, 1130-1(1923).—*Benzal-*asym*-diphenylacetone* (I) (10.8 g. from 11 g. Ph_2CHCOMe and BzH in alc. with aq. KOH in a freezing mixt.), faintly yellowish, m. $102-3^\circ$, sol. in H_2SO_4 with yellow color; like $(\text{Ph}_2\text{CH})_2\text{CO}$, $(\text{Me}_2\text{CH})_2\text{CO}$ and phorone, it is exceedingly stable and dists. without decompn. With Br in CHCl_3 it yields a *dibromide*, m. $147-50^\circ$, gives no color with H_2SO_4 . $\alpha, \alpha, \beta, \delta$ -*Tetraphenyl- β -butanone* (3.6 g. from 3.9 g. I with PhMgBr), m. $89-91^\circ$, gives no color with H_2SO_4 . *Anisal-*asym*-diphenylacetone* (3.6 g. from 3 g. of the ketone), faintly yellow, m. $130-1^\circ$, gives an orange-yellow color with H_2SO_4 . C. A. R.

Action of sodium on β, β -diphenylpropionic ester. D. VORLÄNDER, EDGAR RACK AND WALTER LEISTER. *Ber.* 56B, 1131-5(1293).— $\text{Ph}_2\text{CHCH}_2\text{CO}_2\text{Et}$ (I) b₁₅ $183-5^\circ$; the Me ester m. 48° . I (3 g.) allowed to stand with Na in Et_2O for 4 days gives 2.3 g. *1,1,6,6-tetraphenylhexan-3-ol-4-one* (II), m. $147-8^\circ$, gives no color with FeCl_3 in alc., and 0.2 g. of the *hexane-3,4-dione* (III), yellow, m. $188-9^\circ$, not attacked by cold H_2SO_4 , dissolves on heating with green color, is insol. in dil. aq. acids and alkalis, dissolves easily in NaOH; mol. wt. in boiling C_6H_6 411. If the reaction is carried out in boiling Et_2O , the yields are 0.3 g. II and 0.4 g. III, in boiling C_6H_6 very little II and 0.8 g. III. II (5 g.) heated on the H_2O bath in HNO_3 (d. 1.4) until the evolution of NO ceases yields 1.2 g. III with boiling fuming HI and red P regenerates II. III with CrO_2 -AcOH on the H_2O bath gives chiefly $\text{Ph}_2\text{CHCH}_2\text{CO}_2\text{H}$. *Acetate* of II, m. 93° , gradually dissolves in H_2SO_4 with yellow color changing to orange and then a dirty greenish brown on heating. *Oxime* of II, m. 169° , insol. in Na_2CO_3 sol. in concd. KOH, dissolves in H_2SO_4 with yellow color changing to orange and then Bordeaux-red on heating. *Mono-oxime* of III, sinters about 158° , m. 162° , insol. in dil. KOH and in Na_2CO_3 , sol. in concd. KOH, repdtd. by H_2O , dissolves in H_2SO_4 with yellow color becoming orange and brown on heating. *Dioxime*, m. $211-2^\circ$ (decompn.), sol. in concd. KOH, repdtd. by H_2O , hardly sol. in dil. KOH and Na_2CO_3 . *Phenyllosazone*, dark yellow needles from AcOH or Me_2CO , sinters about 200° , m. 214° , faintly yellowish needles from C_6H_6 -petroleum ether, m. $198-203^\circ$ and changing into the higher melting form in the light or on crystn. from AcOH, becomes brown in the air, gives with H_2SO_4 a dark red color changing to red-brown on heating. *1,1,6,6-Tetraphenyl-3-hexanol*, from II or III in boiling AmOH with Na, m. $139-41^\circ$, sol. in H_2SO_4 with yellow color darkening and finally becoming brown on heating. *1,1,6,6-Tetraphenylhexane*, from II (or III) with Zn dust in boiling AcOH-HCl or with amalgamated Zn in boiling HCl, m. $124-5^\circ$, only slowly attacked by cold H_2SO_4 , dissolves on heating with yellow color becoming brown on higher heating, mol. wt. in freezing C_6H_6 387-91. C. A. R.

β -Phenylbenzalacetophenone. D. VORLÄNDER, JOHANNES OSTERBURG AND OTTO MEYER. *Ber.* 56B, 1136-44(1923).—The following expts. were carried out in the hope of obtaining $\text{Ph}_2\text{C}:\text{C}:\text{CPh}_2$ through the alc. $\text{CH}_3[\text{C}(\text{OH})\text{Ph}]_2$. CH_2Bz_2 with 2 mols. PhMgBr , however, gave only β, β -*di-phenyl- β -hydroxypropio-phenone* (I), m. 119° , also obtained in 14.9 g. yield from 20 g. $\text{CH}_2(\text{CO}_2\text{Et})_2$ and 4 mols. PhMgBr and in 15 g. yield from 20 g. $\text{CH}_2(\text{CO}_2\text{Me})_2$ and 3.5 mols. PhMgBr . It dissolves in H_2SO_4 with reddish yellow color and is decompd. into PhCOMe and Ph_2CO by boiling 20% KOH.

Refluxed with 20% HCl, treated in boiling alc. or AcOH with HCl gas or boiled with AcCl, it gives Ph₂C:CHCOPh (II), yellowish, m. 91°. Like many other closely related substances (Ph₂CHCH:CHPh, Ph₂C:C:CPPh, etc.), II has a tendency to remain liquid in supercooled condition for days and months at room temp., and when crystn. once begins it does not continue unless the thick melt is gently warmed. With PhNHNH₂ in AcOH on the H₂O bath I yields the *phenylhydrazone* of II (also obtained in the same way from II), yellow, m. 222–3°, forms a sky-blue soln. in H₂SO₄ with a few particles of NaNO₂ and is therefore a pyrazolium deriv. (probably tetraphenylpyrazolium). Oxime of II, m. 146°, does not reduce Fehling soln. even on heating, is quite difficultly sol. in KOH but easily in HCl. With Br in CHCl₃ II gives a *mono-Br deriv.*, Ph₂C:CBrcOPh, sinters 155°, m. 168°, sol. in H₂SO₄ with brick-red color; its Br can be completely split off by long boiling with aq. alc. NaOH. With Zn dust in boiling AcOH II gives the *pinacol*, C₂₀H₁₄O₂ (III), m. 192°, of Ph₂CHCH₂COPh, from which III is also obtained with Zn dust and boiling AcOH. Unlike PhCH:CHCOPh, II forms no isolable addn. products of either type A or B (*i. e.*, mol. compds. corresponding to double salts and to complex salts, resp.; cf. *Ann.* 345, 155(1906)) with acids. That A-compds. are apparently formed in small amt. with HCl and H₂SO₄ is indicated by the color changes. Similarly, it practically does not react with CHNa(CO₂Et)₂. *Benzalacetophenone* and *anisalacetophenone bis-hydrosulfates A*, from the ketones and coned. H₂SO₄ shaken several days in cold C₆H₆, orange-brown and red-violet needles, resp. Allowed to stand in Et₂O with PhMgBr, II gives Ph₂C:CHC(OH)Ph₂, m. 138°, which with boiling Ac₂O gives Ph₂C:C:CPPh, m. 164°. Benzalacetylacetone hydrochloride B, m. 105° (*Ber.* 37, 1644 (1904)) does not change in color when dry HCl is passed over it for 5 hrs. at 18° and when 0.5 g. of the product is shaken with H₂O at room temp. and allowed to stand 12 hrs., the filtrate neutralizes only 0.4 cc. 0.1 N alkali; if the HCl treatment is carried out at 0° and –16°, 0.6 and 0.9 cc., resp., of alkali are neutralized; at –80° the substance is turned brown by the HCl and 21.2 cc. alkali is neutralized. PhCH:CAcCOPh reacts with CHNa(CO₂Et)₂ in the usual way, the resulting *hydroresorcinol* m. 128–30°. Anisalacetylacetone likewise forms a *hydrochloride B*, m. 48–50°, which is practically not attacked by H₂O at room temp.; dry HCl turns it reddish, the filtrate, after shaking with H₂O, neutralizing 1 cc. 0.1 N alkali (1.5 cc. if the HCl treatment is carried out at –18°). PhCH:C(COPh)₂ and HCl react with each other but the product cannot be isolated; with CHNa(CO₂Et)₂ the ketone forms a *hydroresorcinol deriv.*, C₂₂H₂₀O₆, m. 54°, acts as a monobasic acid, gives a dark red color in aq. alc. with FeCl₃. C. A. R.

Action of benzene and aluminium chloride on α,β -unsaturated ketones and their halogen derivatives. D. VORLÄNDER AND ALEXANDER FRIEDBERG. *Ber.* 56B, 1144–50 (1923).—In the prepn. of Ph₂CHCH₂COPh from PhCH:CHCOPh (I) with PhMgBr, the latter can be replaced by C₆H₆ and AlCl₃. A comparison of different unsatd. ketones showed that I and benzalmenthone (II), which have a predominating tendency to form with halogen acids addn. products of type B (cf. preceding abstr.), easily react with C₆H₆ and AlCl₃, while *p*-MeOC₆H₄CH:CHCOPh (III), whose *B*-HCl salt is very unstable, does not combine with C₆H₆ and AlCl₃. This indicates that the AlCl₃ reaction does not consist in an addn. of the C₆H₆ to the α,β -double bond but in a substitution by Ph of the β -Cl (or –AlCl₂) group in the *B*-HCl salt first formed. The difference between I and III towards Grignard reagents is less pronounced. Both also form *B*-addn. products with PhSO₂H. In prep. the latter, the preformed PhSO₂H need not be used; a mixt. of C₆H₆ satd. with SO₂ and AlCl₃ can be employed. In other Grignard syntheses with esters, aldehydes and ketones the PhMgBr cannot be replaced by C₆H₆, HCl and AlCl₃. I.HCl reacts much more smoothly with C₆H₆ and AlCl₃ than I itself, 10 g. in 100 cc. C₆H₆ with 30 g. AlCl₃ at 30–40° giving in 10 min. 16.8 g. Ph₂CHCH₂COPh. The I.HCl need not be isolated, 10 g. I in 100 g. C₆H₆ is satd. with dry HCl, heated on the H₂O bath to dissolve the I.HCl which seps., cooled to 40–50° and treated with 30 g. AlCl₃ in small portions; yield of Ph₂CHCH₂COPh, 12.3 g. Ph(*p*-MeOC₆H₄)CHCH₂COPh, easily obtained from III with PhMgBr, m. 91°, is unchanged by boiling Ac₂O, gives a dark red color with coned. H₂SO₄, immediately evolves HBr when treated in cold CHCl₃ with Br, mol. wt. in C₆H₆ 313. α,β -*Triphenylpropio*phenone, m. 182°, mol. wt. in C₆H₆ 328, is obtained in varying yields (depending on the quality of the AlCl₃) from PhCHBr:CHBrCOPh with C₆H₆ and AlCl₃ at room temp., also from α -*bromo- β,β -diphenylpropio*phenone, m. 160–2°, which was prepd. from Ph₂CHCH₂COPh with Br in CHCl₃. II with C₆H₆ and AlCl₃ at room temp. gives *diphenylmethylmenthone*, m. 157°, gives no color with coned. H₂SO₄, mol. wt. in C₆H₆ 275. α -*Benzal- β,β -diphenylpropio*phenone *hydrochloride B* (0.9 g. from 1.5 g. Ph₂CHCH₂COPh in 8 g. BzH satd. at 0° with dry HCl and allowed to stand 3 days at room temp. in a closed vessel), m. 185°, sol. in coned. H₂SO₄ with yellow color and evolution of HCl, does not easily lose its Cl

to C_6H_5N , etc., regenerates Ph_2CHCH_2COPh on heating with C_6H_6 and $AlCl_3$. From I in cold C_6H_6 satd. with SO_2 and slowly treated with $AlCl_3$ is obtained the *benzenesulfonic acid compd.* of I, $C_{21}H_{16}O_2S$, m. 155° , insol. in dil. acids or alkalis, slowly sol. in concd. H_2SO_4 with faint lemon-yellow color changing to dark brown on heating, mol. wt. in $C_{10}H_8$ 343, decompd. by boiling 20% KOH into I and $PhSO_2K$; it is also obtained from I and $PhSO_2H$ in Et_2O ; with $AlCl_3$ in C_6H_6 it gives Ph_2CHCH_2COPh . *Benzenesulfonic acid compd.* of III, m. about 177° (decompr.), unchanged by C_6H_6 and $AlCl_3$ or decompd. on heating. $PhSO_2H$ compd. of $CO(CH:CHPh)_2$, m. $168-70^\circ$, sol. in H_2SO_4 with yellow color changing to red-brown on heating. α, α' -*Didensalcyclopentanonebenzenesulfonic acid compd.*, m. 155° .

C. A. R.
The addition products of the α -unsaturated ketones with mercury halides. D. VORLÄNDER AND EGON EICHWALD. *Ber.* 56B, 1150-2(1923); cf. preceding abstrs.—The following addn. products of type A were prepd.: *Benzalacetophenone-HgCl₂* (6.4 g. from 5 g. of the ketone and 65 g. $HgCl_2$ in the least possible amt. of hot alc.), faintly yellowish, decomp. $92-3^\circ$, decomp. into its components slowly in cold, very rapidly and completely in hot H_2O , also to a large extent in boiling alc.; Br in $CHCl_3$ gives $PhCHBrCHBrCOPh$; the Hg and Cl are pptd. as HgS and $AgCl$, resp., from aq. alc. soln.; fuming HCl gives a small amt. of an orange salt; dry HCl at 0° and 18° adds to a small extent (0.8-1.3% of the added HCl) to form an orange addn. product of type A, the greater part adding to form the B HCl salt with elimination of the $HgCl$. *Benzalacetophenone-HgBr₂* (10.2 g. from 5 g. of the ketone and 8.7 g. $HgBr_2$), yellowish, decomp. $88-90^\circ$, decompd. by C_6H_6 and $CHCl_3$ into the ketone and the bromide. *Anisalacetophenone-HgCl₂*, from the components in $AcOEt$, faintly yellow, decomp. 114° , becomes red with concd. HCl and H_2SO_4 ; *HgBr₂ compd.* (7.5 g. from 4 g. ketone and 6.1 g. $HgBr_2$), yellowish, decomp. $115-7^\circ$. *Dianisalacetone-HgCl₂*, yellow, decomp. about 159° . No addn. products were obtained with phorone, $CO(CH:CHPh)_2$, etc. In the mesityl oxide- $HgCl_2$ compd., the double bond is as sensitive to $KMnO_4$ as in the ketone itself. Neither with $HgCl_2$ nor with $HgBr_2$ was it possible to obtain B-isomers of the above compds.

C. A. R.
Addition velocity of hydrochloric acid to α -unsaturated ketones. D. VORLÄNDER AND EGON EICHWALD. *Ber.* 56B, 1153-6(1923).—Under certain conditions the addn. of HCl to α -unsatd. ketones to form the B-HCl salts (cf. preceding abstrs.) follows the mass law and is accelerated by an excess of HCl. The velocity of addn. in $AcOH$ to $PhCH:CHCOPh$ (I) is 18 times greater than that to $p-MeOC_6H_4CH:CPhCOCH_2Ph$ (II) and this in turn is greater than that to $PhCH:CPhCOPh$ (III). Contrary to the mass law, however, free HCl can also facilitate the dissociation of the addn. product, probably owing to a change in the solvent produced by the dissolved HCl. The expected dimol. course of the addn. reaction could therefore not be followed and the expts. were limited to the measurement of the addn. velocity in the presence of a large excess of HCl. The addns. were carried out in $AcOH$ and the reaction was stopped after measured time intervals by pouring the soln. into H_2O ; the extent to which it had proceeded was measured by detg. the Cl in the resulting ppt. of ketone and its HCl product or by detg. the uncombined HCl in the filtrate from the HCl salt. With I with 1 mol. HCl at $0-20^\circ$, neither the addn. nor the dissociation of the addn. product are sufficiently rapid to be satisfactorily followed analytically. At 65° the dissociation reaction predominates and, within a definite range of concn. of the HCl set free, is accelerated by the latter; equil. is reached, starting either from the addn. product or from I with 1 mol. HCl, at about 10% free I. With about 21 mols. HCl at 16° , $K + K_1 (= (1/f) \log [a/(a-x)])$ is about 0.025 (t in min.) and equil. is reached when 56% of the I has been transformed into the addn. product. With HBr instead of HCl, the results are qual. the same but velocity measurements could not be made because the B-HBr salt crystals out from the $AcOH$ soln. $PhCH:CPhCOCH_2Ph$ adds no HCl after 3 days at room temp. or -18° . For pinene in C_6H_6 with 1.3 or 2 mols. $K + K_1$ falls from 0.00142 after 35 min. to 0.00112 after 305 min.; under these conditions the pinene takes up more than 1 mol. HCl. Attempts to prep. B-addn. products by double decompn. between the B-HCl compds. led to the elimination of HCl or, if the reaction was carried out in alc., to the formation of the alc. addn. products. Thus, the HCl compd. of I with $AgNO_3$ in abs. alc. gave a N-free oil contg. about 60% OEt and the HCl compd. of II gave Hertzka's $EtOH$ compd., m. $92-3^\circ$ (*Monatsh.* 26, 228(1905)); the *MeOH compd.* m. 122° . These alc. compds. dissolve in concd. H_2SO_4 with purple color gradually changing in moist air to blue but stable in sealed vessels, while II itself and its HCl compd. dissolve with yellow-orange color changing to green in the air.

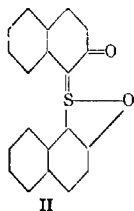
C. A. R.
Pyrogenous catalytic oxidation of naphthalene. I. TOKISHIGE KUSAMA. *Bull. Inst. Phys. Chem. Res. (Japan)* 2, 305-33(1923).—Various conditions for prepn. of

Bz₂O from C₁₀H₈ by pyrogenous catalytic oxidation have been studied. As catalyzers, V₂O₅ and MoO₃ were most suitable; which were better when used mixed with other metallic oxides than when used singly; the best was V₂O₅ contg. a small amt. of MoO₃, which was mixed with asbestos and placed in a glass tube heated in an elec. furnace, through which a mixt. of C₁₀H₈ vapor and air was passed. The temp. of the catalyzer is not homogeneous during the course of reaction, but that of the front part of the catalyzer is generally higher than that of the rear part. The state of reaction is known from the temp. curve drawn by taking the temp. and distance from one end of the catalyzer as ordinates and abscissas, resp. If there is a sharp max. in the front end of the temp. curve, complete combustion of C₁₀H₈ predominates and if the curve shows a gradual rise and a max. at the rear end, it shows that the reaction is going smoothly and a good yield is being obtained. By the form of the temp. curve, the efficiency of the catalyzers and the conditions of the reaction are compared. When a mixt. of V₂O₅ and MoO₃ was used as the catalyzer and air as the source of O₂, complete combustion was minimized by conducting the reaction at 280–400°. When the catalyzer was used in a continuous state, a good yield was obtained by lowering the temp. of the front part of the catalyzer and increasing the velocity of the mixt. of C₁₀H₈ vapor and air. By arranging the catalyzer in parts sepd. by intervals complete combustion is prevented and a good yield obtained.

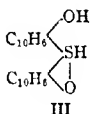
K. KASHIMA

The isomerism of β -naphthol sulfide and analogous isomerisms of aromatic *o*-hydroxy sulfides. RUDOLF LÜSSER AND GEORGE GAD. *Ber.* 56B, 963–78 (1923).—To explain the isomerism of β -naphthol sulfide (I) there is no need of new hypotheses such as that of Hinsberg of "valence centers." Assuming that the dehydro sulfide obtained by oxidizing I has the structure II assigned to it by Hinsberg, its reduction, *i. e.*, the re-addn. of two H atoms, may also proceed in such a way that the 4-membered "thionylum" ring is preserved, one H adding to the S, the other to the doubly bound O atom, with formation of a compd. (III) which should show all the properties of isosulfides (formation of dibasic salts and disubstitution products, easy reconversion into the normal I) and, as a HO mercaptan, should yield two different monosubstitution products and form a disulfide. As a matter of fact, I in Et₂O easily converts it into a disulfide (IV) which on benzylation yields a *dibenzate* (V) and this is reduced by Zn dust and HCl to the *o*-monobenzoate (VI); this in turn is oxidized back quant. to V by I and on the other hand the free IV with Zn dust and AcOH gives III. With 1 equiv. of BzCl, however, III gives the *S*-monobenzoate (VII); on further benzylation both VI and VII give the same *dibenzate* (VIII) of III. The monobenzoate of I is different from either VI or VII; the presence of a free HO or HS group in these 3 compds. was shown quant. by the Zerevitinov method. *6*-Bromo-2-naphthol-1-sulfide (IX) and *Me*, 2,3-hydroxynaphthoate sulfide (X) likewise yield on oxidation red dehydro compds. reduced by Zn dust and acids to isosulfides, but the dehydro compd. from X does not react with PhNHNH₂ or O₂NC₆H₄NHNH₂, and must therefore have the double thionylum ring or "spiran" structure XI, which results when the 2nd *o*-position to the HO group is occupied. These dehydro compds. and isosulfides are not limited to naphthol derivs.; they are formed from aromatic *o*-HO sulfides in which, the *p*-position to the HO group being occupied, there is a tertiary C atom in the *o*-position to the S; thus, they are formed from the sulfides of *p*-chloro-*sym*-*m*-xylenol (XII), *p*-chloro-*p*-xylenol, chlorothymol and 4-cumenol but not from *m*-xylenol and *p*-chloro-*m*-cresol sulfides. A no. of further generalizations were observed in the course of this work. Phenols with a negative substituent in the *o*-position to the HO group do not react at all or at least not under the usual conditions (in CHCl₃, CS₂ or other solvent) with SO₂Cl₂. Again, contrary to the general belief, SO₂Cl₂ does not chlorinate phenols exclusively in the *p*-position; the *o*-compd. is also always formed in varying amts. Finally, S₂Cl₂ or SCl₂ does not react with phenols with a negative substituent in the *o*-position to the HO group when the *p*-position is occupied. *Di*(*iso*- β -naphthol sulfide) (IV), yellow needles with 1 mol. solvent from CHCl₃, begins to decomp. about 128°, m. 141°, light yellow, solvent-free tablets from benzene, m. 141–2°, identical with the product obtained by Hinsberg with H₂O₂. V (8.5 g. from 15.2 g. IV in cold Et₂O with 1.5 times the calcd. amt. of BzCl and an excess of 20% NaOH), yellow tables with 1C₆H₅, m. 202–3°, mol. wt. in PhOH 853–81. VI (2.5 g. from 5 g. V in a little C₆H₆ with Zn dust and HCl under a reflux), yellowish prisms, m. 111–2°. VII (2 g. from 3.18 g. III and 1 equiv. BzCl in cold C₆H₆N), yellowish tablets, m. 181°, sol. in aq. alc. alkalis and reprecip. unchanged by mineral acids. VIII m. 179–80°. *Benzate* of I, m. 190°; *p*-bromobenzoate, m. 195°. IX (85 g. from 21 g. SCl₂ and 89 g. 6,2-C₁₀H₇BrOH in CS₂ under a reflux), m. 245–6°, dissolves with brownish color in excess of hot NaOH and deposits the Na salt on cooling; *dibenzate*, m. 270°. *Dehydro sulfide*, from IX in luke-warm NaOH with K₄Fe(CN)₆, ruby-red, m. 176–7°; *p*-nitro-

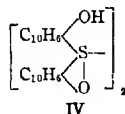
phenylhydrazone, orange-yellow, m. 254° (decompn.). *Isosulfide*, yellowish, m. 156-7°, sol. in warm NaOH with yellow color, being reconverted into **IX**; *dibenzoate*, m. 184-5°. **X** (93 g. from 101 g. 2,3-C₁₀H₈(OH)CO₂Me), lemon-yellow, m. 227-8°; *dibenzoate*, m. 231-2°. *Dehydro sulfide* (**XI**), dark red crystals with golden luster, m. 245-6°. *Isosulfide*, yellow, has the same m. p. as **X** and does not depress that of the latter, so that it undoubtedly passes back into **X** below its own m. p.; *dibenzoate*, yellowish prisms of penetrating odor, m. 176°. **XII**, m. 115-6°, is obtained in 121 g. yield, together with 19 g. of the *o*-Cl isomer, m. 49-50°, from 3,5-Me₂C₆H₃OH and the calcd. amt. of SO₂Cl₂ in CHCl₃; from 61 g. of the xyleneol and 135 g. SO₂Cl₂ is obtained a *di*-Cl compd., 3,5,2,4-Me₄Cl₂C₆H₂OH, m. 95-6°. *Sulfide* of **XII** [5,4,6,2-ClMe₂(HO)C₆H₂]S (25 g. from 31 g. **XII**), odorless needles, m. 214-5°, forms Na and K salts almost insol. in H₂O but easily sol. in alc.; in the calcd. amt. of alc. KOH with 2 mols. Br it gives *p*-chloro-*o*-bromoxyleneol sulfide (**XIII**), m. 215-6°, while 9.6 g. in 2.2 mols. alc. KOH with 16 g. Br yields the *dehydrosulfide* (spiran form) of **XIII**, dark red crystals with velvety luster, m. 195°, reacts with neither PhNHNH₂ nor *p*-O₂NC₆H₄NHNH₂; from the alc. mother liquors H₂O ppts. *o,o'*-dibromo-*p*-chloro-*sym*-*xyleneol*, m. 158°, also obtained from **XII** with the calcd. amt. of Br in AcOH. *Isosulfide* (1.3 g. from 2 g. of the *dehydrosulfide*), yellowish, m. 177°, sol. in aq. NaOH, depositing on boiling a few min. the Na salt of the normal **XIII**, reconverted by Br in alc. KOH into the spiran *dehydrosulfide* and oxidized by I and aq. NaHCO₃ to the *diisulfide*, yellowish, m. 127° (decompn.). *Chloro-*p*-xyleneol*, from the xyleneol in CHCl₃ with SO₂Cl₂, Ag-gray, m. 74-5°; 11.5 g. with 4 g. SCl₂ in CS₂ gives 7.5 g. of the sulfide, [3,3,6,2-ClMe₂(HO)C₆H₂]S, m. 180-1°, sol. in warm aq. NaOH, the cooled soln. giving a yellow-red ppt. with K₃Fe(CN)₆. *Chlorothymol sulfide*, [5,6,3,2-ClMe(C₆H₇)(HO)C₆H₂]S (13 g. from 18.5 g. of *p*-chlorothymol), m. 110-1°, sol. in aq. alc. NaOH and gives a deep red product with K₃Fe(CN)₆ or Br. *ψ-Cumenol sulfide* [3,5,6,2-Me₂(HO)C₆H₂]S (5.5 g. from 8.4 g. *ψ*-cumenol), m. 127-8°; in aq. NaOH with K₃Fe(CN)₆ or in alc. KOH with Br it gives a yellow-red ppt. *m-Xyleneol sulfide*, [3,5,2-Me₂(HO)C₆H₂]S, m. 96-8°, sol. in hot aq. NaOH with yellow color, giving, after cooling, only a yellow-green ppt. with K₃Fe(CN)₆. *p-Chloro-*m*-cresol sulfide*, [5,4,2-ClMe(HO)C₆H₂]S, m. 180-1°, sol. in cold NaOH and gives with K₃Fe(CN)₆ a dirty green product; in the prepn. of the sulfide is formed a by-product, probably the 6,5,2-isomer, m. about 160°, which with K₃Fe(CN)₆ yields a reddish brown ppt.



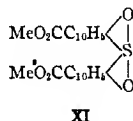
II



III



IV



XI

C. A. R.

Hydroxynaphthoic acids. II. CARLTON BUTLER AND FRANK ALBERT ROYLE. (*J. Chem. Soc.*, 123, 1649-57(1923); cf. *C. A.* 17, 2878).—Using the methods described previously the various HOC₁₀H₇CO₂H have been prepd. from the corresponding H₂N-C₁₀H₆SO₃H. *K* 2-cyanonaphthalene-5-sulfonate, long, friable rods of square cross-section with 4 H₂O; *Na* salt, long, thick prisms with 4 H₂O. *K* salt of the 6-deriv., fine needles with 1 H₂O; *Na* salt, plates with 3 H₂O. *K* salt of the 8-deriv., fine needles with 3 H₂O. *Acid K* salt of 5-sulfo-β-naphthoic acid, long needles with 1 H₂O; *acid Na* salt, needles with 1 H₂O; *acid K* salt of the 6-deriv., small needles with 2 H₂O; *acid K* salt of the 7-deriv., long needles with 1 H₂O; *acid K* salt of the 8-deriv., anhyd. needles. Fusion with KOH gave the HOC₁₀H₇CO₂H in practically quant. yield. 4-Amino-β-naphthoic acid, by distg. H₂NC₁₀H₆SO₃H with K₃Fe(CN)₆, m. 123-4°. Hydrolysis gave 4-amino-β-naphthoic acid, m. 204-6°, from which 4-hydroxy-β-naphthoic acid, m. 182-3°, results upon diazotization. *Ac* deriv., m. 167-8°. 5-HO acid, m. 210-1°; this gives with FeCl₃ a dirty red ppt., turning violet and finally black. *Ac* deriv., m. 214-5°; *Et* ester, m. 150-1°; this gives a yellow color with FeCl₃; *anilide*, m. 163-4°; this acid is identical with that prepd. by Battershall (*Ann.* 168, 144) and Stumpf (*Ann.* 188, 1). 6-HO acid, m. 240-1°; FeCl₃ gives an orange color but no ppt. The Na salt in aq. NH₄OH, KOH or Na₂CO₃ develops a purple fluorescence. *Ac* deriv., m. 221-3°; *Et*

ester, m. 111–2°; FeCl₃ develops a yellow color; *anilide*, m. 197–8°. *γ-HO acid*, m. 269–70°, likewise gives an orange color but no ppt. *Ac deriv.*, m. 209–10°; *anilide*, m. 219–20°. *β-HO acid*, m. 228–9°, gives with FeCl₃ a dirty red ppt. changing through violet to black; the Na, K or NH₄ salt gives a dark green fluorescence in excess alkali. *Ac deriv.*, m. 176–7°; *Et ester*, m. 135–7°; FeCl₃ gives a yellow color, changing to dirty orange and green, a bluish black ppt. being finally deposited. *Anilide*, m. 239–40°; FeCl₃ gives a greenish yellow color. The sulfonation of β -C₁₀H₇(CO₂H) at 100° by means of 98% H₂SO₄ gives rise to 5-, 7-, and 8-sulfo β -naphthionic acids, the 1st predominating. If the temp. of sulfonation is raised to 160°, the main product will be the 7-acid, accompanied by small quantities of the 5- and 8-acids. The 6-acid could not be detected in this operation.

C. J. WISER

Formation of derivatives of tetrahydronaphthalene from α -phenyl-fatty acids.

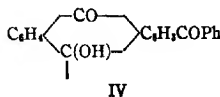
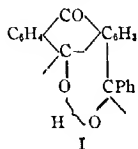
III. The influence of substituents on ring closure. A. J. ATTWOOD, ARNOLD STEVENSON AND J. F. THORPE. *J. Chem. Soc.* 123, 1755–66(1923); cf. *C. A.* 16, 4203.—In order to ascertain more definitely the influence on ring closure of substitution in the β -position, it was decided to compare the effect of other substituents, not only in the β -, but also in the α - and γ -positions. This was done by testing series of isomeric substituted γ -PhCH₂CH₂CH₂CO₂H, each series having the same substituent introduced, if possible, successively in all 3 positions. Of 15 acids tested, 6 yield tetrahydronaphthalene derivs. on treatment with H₂SO₄ at room temp. All 6 have substituents in the β -position, and in addn. a 2nd CO₂H group, which group may or may not form part of the β -substituent. The tests used to det. whether or not condensation had occurred were the formation of semicarbazones and the production of phthalic acid on oxidation. PhCOCH₂CH₂CO₂H was not changed by H₂SO₄, PhCH₂CH₂CO₂H was violently attacked, giving a dark residue, and PhCH₂CH₂CH₂CO₂H gave a brown product, which did not yield a semicarbazone. β -Keto- γ -phenylbutyric acid, decomp. 95° (prepd. from the Et ester, b_m 156°) is very unstable and, on warming or even on exposure to air, loses CO₂ and gives MeCOCH₂Ph. PhCOCH₂C(OH)₂CO₂H (Bromme and Claisen, *Ber.* 21, 1132) is transformed by H₂SO₄ into the dehydrated form which is stable towards H₂SO₄, PhCH₂CH₂CH(CO₂H)₂ and H₂SO₄ gave a brown residue, but this was not a C₁₀H₈ deriv. PhCH₂C(CO₂H)₂CHCO₂H and H₂SO₄ gave 1-ketotetrahydronaphthalene-3,3-dicarboxylic acid (I), m. 170° (decompn.), the semicarbazone of which decomps. 250°. PhCH₂CH(CO₂H)CH₂CO₂H gave 1-ketotetrahydronaphthalene-3-carboxylic acid, m. 149°, also obtained by heating I above its m. p. Semicarbazone, decomps. 261°. PhCOCH₂CH(CO₂H)₂ gave a dark residue which did not yield a semicarbazone. α -Hydroxy- γ -phenyl- α -methylbutyric acid, plates of indefinite m. p., results from PhCH₂CH₂COMe and HCN, followed by hydrolysis. The yield is only 10%. *Ac deriv.*, m. 83°. The acid, with concd. H₂SO₄ decompd. with evolution of gas. *Et β-hydroxy-γ-phenyl-β-methylbutyrate*, b_m 175°; hydrolysis gave a crude acid, which yielded a dark oil with H₂SO₄; this did not yield a semicarbazone.

C. J. WISER

A new class of free organic radicals. III. ROLAND SCHOLL and HERBERT HAUER. *Ber.* 56B, 1065–75(1923); cf. *C. A.* 17, 2709.—The prepn. of benzoylhydroxyanthronyls (I) (the formula in the earlier abstr. is incorrectly printed) by direct reduction of 1-benzoylanthraquinones (II) with metals and concd. H₂SO₄ gives pure products only when their sulfates are difficultly sol. in cold concd. H₂SO₄ and new indirect reduction methods have therefore been worked up by which the I can be obtained easily and quickly in pure cryst. form. The II are first reduced, best with Zn dust and AcOH at low temps., to the anthrahydroquinols (III) which, in accordance with Meyer's "disproportionation" theory (*C. A.* 5, 1408), are converted by acids, slowly at room temp., more or less rapidly at high temps., into the "open" 1-benzoylhydroxyanthronyls (IV) (which under these conditions at once change into the "closed inner-complex" form I) and 1-benzoylanthranols (V), the velocity of the reaction depending on the strength of the acid. On longer continued action of boiling acids, the I are also disproportionated into the II and probably the arylanthraquinonylcarbinols, C₆H₅(CO)₂C₆H₄CH(OH)Ph (VI); this reaction during the prepn. of the I can be repressed, however, by properly adjusting the exptl. conditions (greatly accelerating the main reaction by the use of boiling concd. HCl and CrO₃, rapidly flocking out the I as their green oxonium chlorides with NaCl, and stopping the reaction, which in general is complete in a few sec., by quickly pouring the hot HCl soln. into cold NH₄OH). The CrO₃ effects a direct oxidation of the III and V stages to the I, thus somewhat increasing the yields. 1- β -ClC₆H₄COC₆H₄(CO)₂C₆H₄ with Zn dust and AcOH gives simultaneously the hydro-

quinol and a little of the hydroxyanthrone, C₆H₄ $\begin{array}{c} \text{---CO---} \\ \diagup \quad \diagdown \\ \text{CH(OH)} \end{array}$ C₆H₄COC₆H₄Cl, both of

which, the 1st rapidly, the 2nd slowly, are disproportionated by acids into *p*-chlorobenzoylehydroxyanthronyl (VII) and the anthranol and anthrone, resp., the hydroxyanthrone probably first being isomerized into the hydroquinol. When the alk. $\text{Na}_2\text{S}_2\text{O}_4$ vat of the quinone is treated at room temp. with excess of HCl the free hydroquinol seps. in brown-red flocks and is disproportionated and becomes dark blue only in the course of several hrs. The resulting VII (mixed with other products) is so finely dispersed that it easily forms a colloidal soln. at room temp. in alk. H_2O ; this soln. at once forms a red-brown vat with $\text{Na}_2\text{S}_2\text{O}_4$ which on shaking with air again becomes dark blue, but if the vat is heated a few min. the inner complex ring is ruptured and shaking with air now decolorizes the soln. and ppts. the quinone in light yellow flocks. The velocity with which VII disappears in PhNO_2 under different conditions was followed by titrating with Br; at room temp. in the dark it disappears very slowly (0.6% in 24 hrs.), in diffused light more rapidly (2.7% in 24 hrs.), in sunlight 50% in 1 hr., 100% in 1.75 hrs.; in boiling PhNO_2 under CO_2 in diffused light, 9% in 2 hrs. In these dehydrogenations the I themselves act as the H acceptors. Solns. of *r-p*-toluyl-*g*-hydroxyanthronyl (to be described in a later paper) in dry C_6H_6 under O-free N, as well as PhNO_2 solns., are rapidly decolorized in sunlight, slowly in diffused light, with formation of the quinone but of neither the hydroquinol nor the anthranol; the colorless soln., however, yields to concd. H_2SO_4 a substance which colors the acid an intense brownish red and which is believed to be *p*-tolyl-1-anthraquinonylcarbinol. Similar disproportionations of the I by alkalis, acids and PCl_5 are described. VII, which is obtained in 45% yield from the quinone when the conditions given are followed exactly, forms characteristic deep blue-violet needles with metallic surface luster, m. 253° .



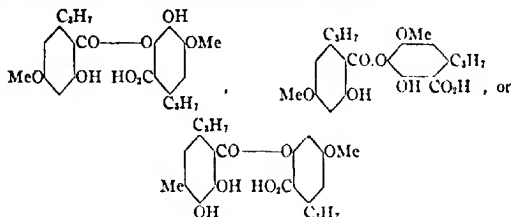
C. A. R.

Furfural from corncobs. F. B. LAForge AND G. H. MAINS. *Ind. Eng. Chem.* **15**, 823-9(1923); cf. C. A. **17**, 1962.—Description of the Bur. of Chem. exptl. plant, having a capacity of 100 lbs. furfural per day.

T. S. CARSWELL

Chemical constituents of a Chinese drug "Shi-hoa" and their constitutions. M. NAKAO. *J. Pharm. Soc. Japan* No. 496, 423-97(1923).—The main constituent of the Chinese drug "Shi-hoa" is *Ramalina divaricata* Ach. var. *obtusata*, Wainio. From an Et_2O ext. of the plant, 3 substances were isolated. (I) Et_2O -sol. (II) difficultly sol. in Et_2O , but sol. in hot C_6H_6 ; and (III) difficultly sol. in Et_2O and hot C_6H_6 . II is usnic acid, $\text{C}_{11}\text{H}_{16}\text{O}_7$, m. $194-5^\circ$ (recrystd. from MeOH) and $195-8^\circ$ (from C_6H_6). $[\alpha]_D^{25}$ 508.3° (CHCl_3). It gives the CHI_3 test, and forms no ester with MeI or MeOH and C_6H_5 . The oxime decomps. 120° , semicarbazone m. 218° , and anilide m. 130° . Heating at 150° with alc. for a few hrs. in a sealed tube gives decarbousnic acid (Knopf), $\text{C}_{11}\text{H}_{14}\text{O}_4$, m. $175-6^\circ$ (Ac deriv. on 115°). By Hesse's treatment II gives usnidic acid, $\text{C}_{14}\text{H}_{18}\text{O}_4$ (IV), m. 197° , $\text{C}_{14}\text{H}_{16}\text{O}$, m. 80° , and $\text{C}_{16}\text{H}_{18}\text{O}_4$, m. 169° . Distn. of IV under 5 mm. gives a yellow oil, from which yellow crystals, $\text{C}_{12}\text{H}_{14}\text{O}_4$, m. 178° , are obtained. This last compd. has exactly the same properties as those of the usnidol of Hesse, except the FeCl_3 test. $\text{Ba}(\text{OH})_2$, or heating in sealed tubes gives no reaction with usnidol. These facts and many other cited support Widmann's formula (*Ann.* **310**, 230; **324**, 139) for II. III, $\text{C}_{12}\text{H}_{16}\text{O}_7$, m. 195° , is not sol. in cold NaHCO_3 . Its properties are identical with those of obtusatic acid prepd. from a European species of a *Ramalina obtusata* by Knopf (m. p. 4° higher than K.'s). On hydrolysis with 2% NaOH, III gives an acid (V) and orcinol, m. 56° (hydrated), and m. 97° (anhyd.); di-Bz deriv., $\text{C}_7\text{H}_6(\text{OBz})_2$, m. $119-20^\circ$. V, m. 210° , gives MeI, β -orcinol and CO_2 with HI, and is named *isorhizonic acid*, 2,5,4-Me₂(MeO) $\text{C}_6\text{H}_2\text{CO}_2\text{H}$. III is therefore a depside of orcellinic acid and V. I, $\text{C}_{22}\text{H}_{32}\text{O}_8$, m. 137° , is sol. in NaHCO_3 ; reddens blue litmus paper in alc., gives a purple-red color with FeCl_3 . It is a new acid, *sekikaic acid*. On boiling with alkali, III gives CO_2 and 2 acids, $\text{C}_{11}\text{H}_{14}\text{O}_4$ VI, and $\text{C}_7\text{H}_6\text{O}_2$ VII. VI m. 148° , is divaricatic acid. It has 1 OH, 1 MeO, and gives MeI, CO_2 and a phenol with HI. This phenol has 2 OH groups, has the same properties as Hesse's divarin, 3,5-(HO) $\text{C}_6\text{H}_2\text{C}_2\text{H}_7$ (except it does not give a purple color with FeCl_3 and m. 76° , while Hesse's m. 82°). Therefore, VI must have the structure 3,5-HO(MeO) $\text{C}_6\text{H}_2\text{C}_2\text{H}_7$. VII, m. 151° , is hydroxy-

divaricating acid and gives CO_2 , MeI and hydroxydivarin with HI. Thus I is a depside of VI and VII and must have one of the following formulas.



S. T.

Some transformations of 2,4-dimethylpyrrole. HANS FISCHER, BERNHARD WEISS AND MAX SCHUBERT. *Ber.* 56B, 1194-202(1923).—From 0.9 g. 2,4-dimethylpyrrole (I) and 0.8 g. MeCN in cold Et_2O satd. with dry HCl and allowed to stand 1 day is obtained 0.7 g. of the *ketimine*, m. 100°, sublimes 100° (*HCl salt*, green needles), of 2,4-dimethyl-5-acetylpyrrole (II). The ketimine is reduced by H and Pt sponge in alc. to I and when boiled with H_2O to disappearance of the NH odor, 0.7 g. of it gives 0.3 g. II, m. 121°. 2,4-Dimethyl-5-chloroacetylpyrrole (0.9 g. from 1 g. I and 1 g. MeCN in cold Et_2O satd. with dry HCl and allowed to stand 0.5 hr. in ice), m. 143°, gives in alc. with 30% NHMe_2 after 0.5 hr. at 100° the 5-dimethylaminoacetyl deriv., m. 110°, while 0.5 g. boiled 0.5 min. in alc. with 40% HCHO and a few drops coned. HCl yields 0.4 g. *bis*-[2,4-dimethyl-5-chloroacetylpyrrolyl]methane, m. 258°, which with NHMe_2 in alc. gives the *bis*-5-dimethylaminoacetyl deriv., m. 170°. I (1 g.) boiled up several times with 2 g. of 90% HCO_2H and 10 drops of 20% HClO_4 and allowed to stand 1 day gives 0.5 g. of the perchlorate, becomes discolored 200°, does not m. 260°, of *bis*-[2,4-dimethylpyrrolyl]methane, yellow, m. 117°. 2,4-Dimethyl-5-carbethoxy-pyrrole (III), obtained in 80-70% yield from I and EtMgBr and subsequent treatment with ClCO_2Et , m. 125°, gives a positive Ehrlich aldehyde reaction in the cold, is hydrolyzed by boiling 50% KOH to the free acid, m. 136°, also obtained from the above Grignard compl. with CO_2 . 2,4-Dimethyl-5-carbethoxy-pyrrole-3-aldehyde (IV), obtained in 85% yield from III and HCN in cold Et_2O satd. with dry HCl and subsequent decompn. of the resulting imide chloride with hot H_2O , m. 145°, gives a faint Ehrlich aldehyde reaction in the cold, more strongly on heating; 3 g. heated with 1:1 KOH until completely dissolved (about 15 min.) gives 2.2 g. of the free 5-carboxyaldehyde, m. 230°, which on distn. *in vacuo* yields 2,4-dimethylpyrrole-3-aldehyde, m. 126°, gives a positive aldehyde reaction even in the cold. Phenylhydrazone of IV, m. 204°. Azlactone, $\text{C}_{10}\text{H}_{13}\text{O}_4\text{N}_2$ (1.3 g. from 1.2 g. IV, 1.8 g. hippuric acid, 2.2 g. NaOAc and 20 cc. Ac_2O heated 35 min. on the H_2O bath), m. 232°. Oxime, m. 196-7°, converted by boiling NaOAc- Ac_2O into the nitrile, $\text{C}_{10}\text{H}_{11}\text{O}_2\text{N}_2$, m. 171°. Semicarbazone, m. 285° (decompn.), converted by Na in alc. after 8 hrs. at 160-70° into 2,3,4-trimethylpyrrole. 2,4-Dimethyl-5-carbethoxy-3-chloroacetylpyrrole, from III and ClCH_2CN , m. 163°, gives a faint positive Ehrlich reaction on heating, is highly sternutatory when powdered, gives in boiling alc. with aq. KCN the 3-cyanoacetyl deriv., m. 172-3°.

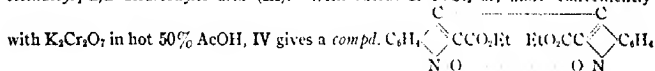
C. A. R.

Synthetic experiments with blood pigment cleavage products and complex salt formation in dipyrrolymethenes. I. HANS FISCHER AND MAX SCHUBERT. *Ber.* 56B, 1202-11(1923).—Hitherto, all attempts to use the degradation products of the blood pigment for synthetical purposes have led only to the formation of bimol. pyrroles with the same substituents on both nuclei and since in bilirubic acid has been found a combination of a basic hydroxypyrrrole with a pyrrolocarboxylic acid it became most important to prep. a combination of a basic blood pigment deriv. with an acid component. Kryptopyrrole (I), which was then to be converted into the aldehyde, was chosen as the starting point but as it is obtained in only 20% yield by the methods of synthesis previously used it was hoped that better results might be obtained by starting from a crust. substance, such as 2,4-dimethyl-3-acetylpyrrole semicarbazone, m. 203-4°, which could then be reduced to I with hot NaOEt, but the semicarbazone was obtained in only 0.1 g. yield from 0.5 g. of the ketone. 2,4-Dimethyl-3-acetyl-5-carbethoxy-pyrrole hydrazone, m. 137°, is smoothly obtained, however. Nor need it be isolated; when 6 g. of the ketone is heated 8 hrs. on the H_2O bath with 3 g. $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$, then 12 hrs. at 150-80° with 5 g. Na in 75 cc. alc., then distd. with steam and the distillate is extd. with CHCl_3

there is obtained 2.1 g. crude I, yielding 5.5 g. of the picrate, m. 136°. From the part non-volatile with steam can be isolated considerable 2,4-dimethyl-3-acetylpyrrole ketazine, m. 212° (picrate, m. 208°). 2,4-Dimethyl-3-ethyl-5-chloroacetylpyrrole, from the crude I and ClCH_2CN in cold CHCl_3 satd. with HCl and allowed to stand 12 hrs., m. 149°, gives a negative reaction with Ehrlich's reagent in the cold, positive on heating, yields with alc. NHMe_2 in a sealed tube at 100° the HCl salt, m. 201-2°, of the 5-dimethylaminoacetyl deriv. *C-Kryptopyrrolmethylamine* (1 g. from 1 g. I and 0.75 cc. anhyd. HCN in cold CHCl_3 satd. with dry HCl and allowed to stand 1 day), m. 142°; 1 g., boiled in H_2O suspension to disappearance of the NH_2 odor yields 0.1 g. 2,4-dimethyl-3-ethyl-5-formylpyrrole (II), m. 105-6°. Oxime of II, m. 118°, yields a picrate, m. 155°. Semicarbazone, m. 203°; picrate, m. 162°. From 0.6 g. of the semicarbazone heated with Na in alc. at 150-60° for 7 hrs. is obtained phyllopyrrole, isolated as the picrate (0.4 g.), m. 104°. Equimol. amts. of II and 2,4-dimethyl-3-carbethoxypyrrrole (III) boiled a short time in a little concd. HCl yield the HCl salt, m. 212°, of bis-[2,4-dimethyl-3-carbethoxypyrryl]methene, m. 189°. Bis-[2,4-dimethyl-3-ethylpyrryl]methene perchlorate, from II in a little alc. and 20% HClO_4 heated to incipient boiling and allowed to stand several days, becomes discolored 170°, decomps. 240°. With 1 mol. kryptopyrrolecarboxylic acid instead of III, however, 0.06 g. II gives 0.04 g. of the brown-red HCl salt of [2,4-dimethyl-3-propionic acid-pyrryl][2,4-dimethyl-3-ethylpyrryl]methene (IV), m. 215°, and with hemopyrrolecarboxylic acid is obtained the HCl salt of [3-propionic acid-4,5-dimethylpyrryl][2,4-dimethyl-3-ethylpyrryl]methene (V), m. 220°. Complex Cu salts were obtained from the following methenes in alc. with ammoniacal Cu soln.: Bis-[2,4-dimethylpyrryl]methene, $\text{C}_{22}\text{H}_{30}\text{N}_4\text{Cu}$ (0.2 g. from 0.5 g. of the methene), green needles, mol. wt. in boiling C_6H_6 440, shows in very dil. CHCl_3 soln. an absorption band at $\lambda 490-515$, changed by AcOH to green with production of a band at $\lambda 480-50$; when the soln. is shaken with concd. HCl the latter becomes faintly pink and shows a faint absorption at $\lambda 500-485$, while the CHCl_3 soln. shows sharp absorption at $\lambda 500-450$. Cu salts of IV and V, red-brown needles. Cu salt of bis-(hemopyrrolecarboxylic ester)-methene, crystals with a green shimmer, shows a sharp absorption band in very dil. alc. soln. at $\lambda 520-10$. 2,4-Dimethyl-3-acetylpyrrole-5-carboxamide (0.8 g. from 4 g. of the Et ester heated 6 hrs. at 150-60° with concd. NH_4OH), m. 260°. C. A. R.

o-Nitrobenzylacetoacetic ester and its transformations. S. GABRIEL, WILH. GERHARD AND R. WOLTER. *Ber.* 56B, 1024-36(1923).—Et *o*-nitrobenzylacetoacetic (I), from 13 g. $\text{AcCH}_2\text{CO}_2\text{Et}$, 2.3 g. Na and 8.5 g. *o*- $\text{O}_2\text{NC}_6\text{H}_4\text{CH}_2\text{Cl}$ in alc. after 2 days, faintly brown-yellow, b_p about 180°, gives a cherry-red color with FeCl_3 . When the crude product (which contains some of the di- $\text{O}_2\text{NC}_6\text{H}_4\text{CH}_2$ deriv. (II)) is shaken 10-5 min. with cold 3% KOH, the II remains undissolved and the filtrate on acidification deposits a gray-brown ppt. sepd. by extrn. with petroleum ether into the insol. *N*-hydroxyindole- α -carboxylic acid (III), m. 159.5°, and its sol. Et ester (IV), m. 64-5°; yield of IV, 12 g. from 34 g. $\text{O}_2\text{NC}_6\text{H}_4\text{CH}_2\text{Cl}$. IV is volatile with steam and can also be distd. *in vacuo*; it dissolves in cold dil. alkali with yellow color and with excess of KOH forms a lemon-yellow K salt which is quickly hydrolyzed in H_2O at 100° into III; IV is insol. in dil. NH_4OH but with alc. NH_3 it forms an unstable lemon-yellow NH_3 compd. Solns. of IV in H_2O or dil. AcOH become yellow, then red and finally dark brown when treated with HNO_3 or FeCl_3 and deposit a brown powder with greenish shimmer, also obtained with $\text{K}_2\text{Cr}_2\text{O}_7$ in AcOH, the soln. in this case becoming violet. The Me ester, m. 100-1°, behaves in the same way, but the phenomenon is not exhibited when the HO on the N is alkylated. With 2 *N* NaOMe and MeI at 100°, IV gives Me *N*-methoxyindole- α -carboxylate, m. 63-4°; with NaOEt and EtI, Et *N*-ethoxyindole- α -carboxylate and the Na salt of the free acid, m. 150-1°. *N*-Benzylindole- α -carboxylic acid, from IV, NaOMe and PhCH_2Cl in MeOH in a sealed tube, m. 168-9° (decompn.); at the same time is formed its Me ester, m. 82-3°; Et ester, m. 77-8°. Benzole of IV, m. 104-5°; acetate, m. 76-7°; di-Cl deriv., from IV and Cl in CCl_4 , yellowish, m. 98-9°; bromination in C_6H_6 gives a mono-Br deriv., m. 82-4°, and in AcOH a tri-Br deriv., m. 138.5°. From 3.6 g. IV with 3.4 g. crystd. SnCl_4 in 4 cc. each of AcOH and fuming HCl below 60° is obtained 2.8 g. Et indole- α -carboxylate (V), m. 125-6°; distils without decompn., is volatile with steam, insol. in cold alkali, also obtained from IV with colorless HI and a little PH_4 on the H_2O bath or with SO_2 or $(\text{NH}_4)_2\text{S}$ in alc. at 100°; free acid (VI), m. 203°, dissolves in boiling SOCl_2 with formation of the yellow chloride and the yellow anhydride, m. 312-5°. With $\text{BrC}(\text{NO}_2)_2$ in MeOH or C_6H_6 , V gives Et β -bromoindole- α -carboxylate, yellowish, m. 152-3°, hydrolyzed by warm 10% KOH to the free acid; m. 199° (decompn.). With PCl_5 on the H_2O bath, V yields Et β -chloroindole- α -carboxylate, m. 153-4°; if the mixt. of V and PCl_5 is fused the product is a di-Cl deriv., m. 194-5°. Free β -Cl acid, m. 180-2° (decompn.), distils unchanged *in vacuo*, reduced

by HI and PH_4I on the H_2O bath to VI. IV in warm 50% AcOH with 10% FeCl_3 gives *di-Et* β,β' -bis-[*N*-hydroxyindolyl]- α,α' -dicarboxylate (X), m. 152-3°, sol. with lemon-yellow color in cold alkalis and reprecipitated by AcOH (excess of KOH ppts. the *K salt*), sol. in NH_4OH , forms in concd. H_2SO_4 an indigo-blue soln. becoming dirty brown on warming and yielding a red-violet ppt. with H_2O , sol. in warm AcO with deep red color; further oxidation with FeCl_3 gives the compd. VII (below) and reduction yields VIII; with alk. Me_2SO_4 is obtained the *di-Me ether*, softens 126°, m. 129°; KOH at 110° yields the free acid, ochre-colored, decomp. 250-70°, forms in soda or NH_4OH yellow solns. which soon darken in the air, is partly reduced by fusion with KOH to [β,β' -bisindolyl]- α,α' -dicarboxylic acid (IX). With excess of FeCl_3 or, more conveniently



(VII), cantharides-green leaflets, brown-red in incident light, m. 189° (decompn.), converted into X by mixing with 2 mols. IV in hot AcOH, reduced in hot AcOH or HCl by SnCl_2 to the *di-Et ester* (VIII) of IX (also obtained from X with HI- PH_4I on the H_2O bath, by heating with PCl_5 or best with SnCl_2 in AcOH-HCl on the H_2O bath), m. 225-6°, converted in boiling alc. by 33% KOH into the *di-K salt*, $\text{C}_{20}\text{H}_{17}\text{K}_2\text{N}_4\text{O}_4\text{H}_2\text{O}$ (the *NH_4 salt* was also prepd.), of the free acid (IX), cryst. powder with H_2O , m. above 285° when slowly heated (probably decomp. into the compd. XI), loses its H_2O in a high vacuum at 150-60°; *dichloride*, obtained by boiling with SOCl_2 , lemon-yellow, reddens 170-80°, does not m. 290°, gives with hot MeOH the *di-Me ester*, faintly yellowish, sublimes on cautious heating and m. 318-20°. Heated under 1 mm. up to 280°, IX loses CO_2 and H_2O and gives α -[bisindolyl] (XI), m. 286.7° in a sealed capillary, sublimes on strong heating in a high vacuum, gives in hot AcOH with a drop of fuming HCl a raspberry color which disappears on boiling and returns on cooling, mol. wt. in Me_2CO 245-59, converted into the β -isomer (XII) by boiling in AcOH with HI or HBr but not with HCl. Boiled several hrs. with HI-AcOH as in the Zeisel method for detg. alkyl groups, X loses hardly 0.5 of its Et, forming a tobacco-brown *prindide* which, on further short heating after addn. of PH_4I , changes into a lemon-yellow *III salt* from which excess of alc. NH_3 liberates *Et* [β,β' -bisindolyl]- α -monocarboxylate, light yellow, m. 172.3°; free acid, chrome-red needles with 0.5 H_2O , m. 209-10°, dissolves in NH_4OH without color and seps. unchanged on spontaneous evapn., loses CO_2 and H_2O , with formation of XI, after several hrs. at 200° under 0.4-0.5 mm. If to the mixt. of X and HI-AcOH, PH_4I is added to combine with the I set free, both CO_2Et groups can be split off, with formation of a yellow *III salt* (also obtained from IX in boiling AcOH-HI), converted by excess of alc. NH_3 into XII, m. 207-8°; *HBr salt*, lemon-yellow. Whether the isomerism of XI and XII is due to the double bonds being in different positions remains to be detd. The Me ester of III likewise yields with FeCl_3 a yellow *di-Me ester*, sinters about 160°, m. 209-10° (decompn.), corresponding to IV, with $\text{K}_2\text{Cr}_2\text{O}_7$ a *red-brown compd.* ($\text{C}_{12}\text{H}_7\text{NO}_2$)₂, which is cantharides-green by reflected light, and with SnCl_4 the *di-Me ester*, m. 318-20°, of IX. C. A. R.

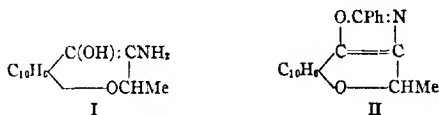
Preparation and bromine reaction of tryptophan. MAX STEGELMANN. *Beitr. Physiologie* 2, 5-6; *Chem. Zentr.* 1922, III, 555.—The Hg ppt. obtained by Hopkins and Cole was decompd. by HCl, the free acid removed from the soln. by PbO, the PbO with H_2S , the HCl residue with Ag_2CO_3 and the Ag residue with further treatment with H_2S . The Br reaction of tryptophan is changed to a blue by the addn. of excess $\text{C}_6\text{H}_5\text{N}$ and the dye can then be extd. with AmOH or EtOAc. C. C. DAVIS

Indine and isoindigo. O. DORNIER AND JH. MARTINET. *Bull. soc. chim.* 33, 779-86(1923).—The literature on the indine of Laurent (β -indine of Knopp), the ω -indine of Knopp and the isoindigo of Wahl is reviewed. The three compds. prepd. by original methods were found identical through examn. of their absorption spectra in the ultra-violet. The spectrum of the second showed minor variations identical to those produced by traces of indirubin. The latter is tentatively postulated an intermediate product in the reaction of dioxindole with glycerol to give the α -indine of Knopp. R. L. BROWN

Pyrylium compounds. XII. Constitution of the methyl-diphenylpyrylium salts. W. DILTHEY AND J. FISCHER. *Ber.* 56B, 1012-3(1923); cf. *C. A.* 16, 3900.—Since the methyl-diphenylpyridine, m. 72-3°, obtained from the methyl-diphenylpyrylium salts (I) (*C. A.* 11, 450) with NH_3 was apparently different from v. Meyer's 2-methyl-4,6-diphenylpyridine, m. 156°, it was concluded that the I are the 4-methyl-2,6-diphenyl compds., but subsequently Gastaldi, on the basis of their conversion into the CO_2H acid (*Chem. Zentr.* 1922, III, 778), and Schneider and Ross, on that of their formation

from dypnone (C. A. 17, 1013) concluded that the Me is in the α -position of the pyridine nucleus. D. and F. believe that a better proof of the correctness of the views of these authors is afforded by the fact that the I heated with 1.5 mols. BzH yield a compd. identical with that obtained by the condensation of PhCH:CHCOPh with PhCH:CHCOMe, which can be only a 2-styryl-4,6-diphenylpyrylium deriv. C. A. R.

The ammonia addition product of 2-methyl-(β -naphtho- α -chromone). WILHELM SCHNEIDER and HELMUTH BODE. *Ber.* 56B, 1042-6(1923).—The yellow by-product $C_{14}H_{11}O_2N$ (I) obtained in the prepn. of 2-methyl[β -naphtho- α -chromone] (II) from its Ac deriv. (III) with alc. NH_3 (C. A. 16, 1248) can under the proper conditions be made the chief product of the reaction (8.2 g., together with 2.8 g. II, from 11 g. III in abs. alc. suspension treated with NH_3 gas until the III dissolves, allowed to stand overnight well stoppered, freed from most of the NH_3 with air, filtered from the I which seps. (5.5 g.), dild. with several vols. H_2O , treated with cold dil. NaOH, filtered from the undissolved II and treated with CO_2 which ppts. 2.7 g. more of I); it m. 138-9°, dissolves in most org. solvents with yellow color, gives an intense dark green color in alc. or Et_2O with $FeCl_3$, dissolves in alkalis with yellow color and in not too dil. mineral acids without color; from the acid solns., if they have not been warmed and have been freshly prepd., I is repptd. unchanged when the acidity is toned down, but on long standing in acid soln., more quickly on warming, it decomps. into NH_3 and II. Picrate of I, yellow, m. 179-80°, easily decomps. in soln. into NH_3 picrate and II. I cannot be prepd. from the free II instead of III with NH_3 in alc. or C_6H_6 . With alk. Me_2SO , I yields a Me ether, m. 198°, sol. in not too dil. mineral acids with yellow color, repptd. by alkalis, gives no color with $FeCl_3$, sol. in concd. H_2SO_4 with intense yellow color; picrate, yellow, m. 171°. The properties of I are satisfactorily explained on the assumption that it is 2-methyl-3-amino-[α -naphtho- β -chromen-4-ol]. With BzCl in dil. NaOH it gives a phenylloxazole deriv. (IV), yellowish, m. 137°, insol. in NaOH and dil. acids, very stable towards hydrolytic agents, being unchanged by boiling dil. alkalis and acids and assuming a yellow color only when warmed with concd. NaOH.



C. A. R.

The action of organic magnesium compounds on nitriles. P. BRUYLANTS. *Bull. sci. acad. roy. Belg., Classe de sci.* 8, 7-23; *Chem. Zentr.* 1923, I, 85-6; cf. Moureu and Mignonaç, *Ann. chim.* [9] 14, 322.—The action of Grignard's reagent on $CH_2(CH_2CN)_2$ to give a complicated product (cf. C. A. 16, 3647) is applied to MeCN (I). I acted like a pseudo-acid and liberated the hydrocarbon. From MeMgBr and EtMgBr the corresponding N-MgBr compds. were obtained. The latter, without neutralizing, were decompd. with the least possible H_2O (in a few cases with EtOH) and extd. several times with Et_2O . The first Et_2O ext. sepd. in a small yield as crystals (II). The residual exts. were fractionated at 15 mm., whereby first NH_3 and H_2O distd., then at 130-50° a sirupy compd. (III) and at 150-70° an oil. From the latter a compd. (IV) crystd. The residual oil on steam distn. gave a solid (V). II had a mol. wt. 135, with approx. formula $C_4H_7N_3$ by combustion, m. 198-200°, was insol. in cold H_2O and liberated NH_3 in warm H_2O , giving another compd. (VI), m. 135°. III gave a semicarbazone, m. 164° (cor.), identical with the semicarbazone of $AcCH_2CN$ (cf. Holzwardt, *J. prakt. Chem.* 39, 230). IV, $C_8H_8N_2O$, m. 209° (decompn.), is identical with 2,4-dimethyl-6-hydroxy-3-cyano-pyridine (V) (cf. *J. Chem. Soc.* 81, 100(1902)). IV gave an unexplainable approx. mol. wt. of 190 (calcd. 148). V m. 123°, mol. wt. 118, sublimed at 50°, had a bitter taste, formed a base, probably $C_7H_7N_3$, which pptd. most alkaloïds. HCl salt. Chloroaurate, m. 103°. The chief product was V, formed during the distn. by the action of H_2O on the diacetonitrile, which is the primary product of the reaction. In the ext. freed from II it could be detected before distn. but diacetonitrile semicarbazone, m. 225° (cf. *J. prakt. Chem.* 78, 505), was isolated. The original Et_2O ext. dried over KOH gave on distn. *in vacuo* the diacetonitrile, b. 160-80°, m. 75-7°, m. (after recrystn. from C_6H_6) 67-78° (cf. *J. prakt. Chem.* 52, 84; 78, 497). Mono-Br deriv. m. 123-5°. The fraction b. 180-260° (*in vacuo*) of the ext. dried over KOH, solidified completely and was approx. $C_8H_8N_2$, m. 158-60°, b. 298-300° (cor.), pptd. from H_2O by NaOH, identical with 2,4-dimethyl-6-amino-3-cyanopyridine. The expected reaction product, MeEtCO (cf. *Compt. rend.* 132, 38; 133, 299) was not detected.

The reactions are assumed to proceed thus (the MeCN acts as a pseudo-acid, $\text{MeCN} \rightleftharpoons \text{CH}_2:\text{C}:\text{NH}):\text{CH}_2:\text{C}:\text{NH} + \text{RMgBr} \rightarrow \text{RH} + \text{CH}_2:\text{C}:\text{NMgBr}$, $\text{CH}_2:\text{C}:\text{NMgBr} + \text{MeCN} \rightarrow \text{MeC}(\text{NMgBr})\text{CH}_2\text{CN} \rightarrow \text{MeC}(\text{NH})\text{CH}_2\text{CN} \rightleftharpoons \text{MeC}(\text{NH}_2):\text{CHCN} \rightarrow \text{MeC}(\text{OH}):\text{CHCN}$. $\text{MeC}(\text{OH}):\text{CHCN} + \text{CH}(\text{CN}):\text{C}(\text{OH})\text{Me} \rightarrow \text{H}_2\text{O} + \text{V}$.

C. C. DAVIS

The pepper taste of piperine. HEINRICH RHEINBOLDT. *Ber.* 56B, 1228-9(1923).—In view of the belief of Oit and Zimmermann (*C. A.* 16, 1220) that the sharp taste of piperine (I) in alc. is not due to I itself but to the presence of the pepper resin, the last traces of which are very difficult to remove, R. purified the I through the SnBr_3 salt and found that the crystals of I so obtained, although having only a faint pepper taste when bitten into, have an extraordinarily sharp and biting taste in alc. The SnBr_3 compd. likewise has a strong pepper taste and this is especially true of the mixt. of SnO and I obtained by decomg. the double salt with NH_4OH , which contains the I in a very fine state of subdivision. These results therefore confirm the findings of Staudinger and Schneider (*C. A.* 17, 2581).

C. A. R.

Hydrolysis of scopolamine. RICHARD WILLSTÄTTER AND ENDRE BEKNER. *Ber.* 56B, 1079-82(1923).—According to the investigations of Cadamer and Hammer (*C. A.* 15, 3118) and of Hess and Wahl (*C. A.* 17, 397), the basic component (I) of scopolamine (II) (which, following a suggestion of Eykman, is designated *scopine*) is yet unknown, the known scopoline (III) being formed from it by rearrangement of the α -oxide into a γ -oxide ring. Usually tropeines are hydrolyzed, mixed with olive oil, by means of pancreas lipase in the presence of an $\text{NH}_2\text{NH}_2\text{Cl}$ buffer, but lipase is not a satisfactory agent for this purpose and comparative expts. at 30° with the buffer alone (pH 8.9-9.0) showed that II is hydrolyzed 62, 80 and 97% in 9, 13 and 35 days, resp. During such long continued action, however, the I partly rearranges into II and it is difficult to sep. the 2 bases. I can be obtained pure when the hydrolysis is stopped earlier and the difficultly sol. unchanged II is filtered off. On heating and under the action of acids and alkalis, I changes easily into III. Thus far, it has been obtained in only 1 of the 4 possible geometrically isomeric forms. From 34 g. II in 500 cc. NH_4Cl and 250 cc. of 0.5 N NH_3 kept 9 days at 30° were obtained 14.35 g. unchanged II (contg. some I), 11.6 g. tropic acid and 8.0 g. I. I m. 76° , is optically inactive, does not react with $\text{NH}_3\text{-AgNO}_3$, stands in its behavior towards $\text{CrO}_3\text{-H}_2\text{SO}_4$ at 50-60° midway between the easily oxidized tropine and the difficultly oxidized III, a large part of it being recovered as III. It is more stable towards acids than towards alkalis, being unchanged by N HCl in 24 hrs. at room temp. while by N KOH it is almost completely isomerized into III in 24 hrs., although hardly changed at all in 1 hr. When it is heated under atm. pressure III (contg. a little I) dists. over at 248° and the residue consists of pure III. It can be heated without change 1 min. at 150° ; after 5 min. the m. p. falls to 65° ; at 200° , much III is formed in 5 min. *HCl salt.* *Picrate*, m. 231° (decompn.). *Chloroplatinate*, prisms with $2\text{H}_2\text{O}$, m. 219° (decompn.) (the *chloroplatinate* of III, tables with 1 H_2O , m. 203° (decompn.)). *Chloraurate* of I, prisms with $1/2$ mol. H_2O (air-dried), m. 216° (decompn.); of III, ppt. of prismatic tablets with 0.5 H_2O (anhyd. prisms from hot H_2O contg. a little HCl), m. 220° (decompn.).

C. A. R.

Propiopapaverine and homocoralyne. WILHELM SCHNEIDER AND ERHARD NITZE. *Ber.* 56B, 1036-41(1923).—It was shown (*C. A.* 15, 62) that papaverine (I) with Ac_2O contg. $\text{HOSO}_2\text{CH}_2\text{CO}_2\text{H}$ yields an acetopapaverine (II, R = Me) which, however, has the properties of a pseudo base and is isolated from the reaction mixt. as the sulfoacetate of the isomeric quaternary NH_4^+ base, coralyne (III). It has now been found that with $(\text{EtCO})_2\text{O}$ instead of Ac_2O is obtained the sulfopropionate of a *homocoralyne* (IV) and that the free IV changes with extraordinary ease, even in the cold, into the H_2O insol. pseudo base, *propiopapaverine* (V), i. e., the relative stabilities of the 2 isomers are in this case just the opposite of those of II and III. Similarly the chloride of IV is decomp. by dil. NaOH into V while from that of III the III is merely salted out unchanged. *Sulfopropionate* of IV, $\text{C}_{22}\text{H}_{34}\text{O}_6\text{NSO}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{H} \cdot 1.5\text{H}_2\text{O}$, obtained in 12.5 g. yield from 10 g. I heated 15 min. at 85° with a mixt. of 8 cc. concd. H_2SO_4 and 100 cc. $(\text{EtCO})_2\text{O}$ which has previously been heated at 85° until it no longer reacts with BaCl_2 , yellow needles, m. 273° (decompn.), shows intense yellow-green fluorescence in org. solvents; *chloride*, yellow needles with 3 H_2O , m. 250° (decompn.); *iodide*, yellow needles with 1 H_2O , m. 268° (decompn.); *nitrate*, yellow needles with 2 H_2O , sinters above 273° without melting; *acid sulfate*, $\text{C}_{22}\text{H}_{34}\text{O}_6\text{NS} \cdot 2.5\text{H}_2\text{O}$, yellow gelatinous ppt., gradually decomps. above 300° ; *perchlorate*, yellow cryst. ppt. with 1 H_2O , gradually decomps. above 280° ; *picrate*, intensely bright yellow cryst. ppt. with 2 H_2O , m. 259° (decompn.). V, yellowish white, m. $145-6^\circ$; *phenylhydrazone*, m. $205-6^\circ$; *oxime*, m. 212° ; *methiodide* (1.5 g. from 1.1 g. V heated 3 hrs. at 100° with MeI in C_6H_6), yellow, m. $215-6^\circ$, converted by

dil. NaOH into *N*-methylpropioisopaverine, $C_{14}H_{17}O_4N$, yellow amorphous powder, m. 120.4°. With Zn in boiling dil. H_2SO_4 + AcOH and subsequent addn. of KI the sulfopropionate of IV gives a faintly yellow iodide, m. 217°, from whose aq. soln. NH_4OH ppts. intensely yellow amorphous flocks of a base entirely similar in its properties to dihydrocoralyn (*C. A.* 16, 1098), becoming, when moist, orange-yellow in the air; not enough was available, however, for purification and more detailed study. *Hexahydrohomocoralyn (homocoralydine) hydriodide*, from the sulfopropionate refluxed 24 hrs. with Zn in dil. H_2SO_4 + AcOH, then nearly neutralized with NaOH and treated with KI, m. 236°; free base, m. 145.6°, gives a faint greenish color with hot concd. H_2SO_4 .
C. A. R.

Simultaneous existence of optically active asparagines in germinated lupines (PUTTI) 11A. Preparation of creatinine from creatine (EDGAR, HINEGARDNER) 11B. The hydrogenation potential of aloxanthine (BIHMANN, LUND) 2. The nature of the non-polar link (SIDGWICK) 3. Magnetic properties of cyanic and cyanuric derivatives (PASCAL) 2. The valence energy of hydrocarbons (WIBAUT) 2.

Urea. Soc. D'ETUDES CHIMIQUES POUR L'INDUSTRIE. Brit. 192,703, Feb. 1, 1923. Urea is obtained from solns. of cyanamide by treating with an acid, in quantity less than 10% of that necessary to combine with all the urea produced, at a temp. below 65° and under pressure; suitable acids are H_2SO_4 , HNO_3 , or H_3PO_4 , or salts such as $NaHSO_4$. An example is given in which a soln. of cyanamide is heated at 65-70° for 6 hrs. in a Pb lined autoclave under a pressure of 5 atm. produced by an inert gas such as N.

Carbazole derivatives. NATIONAL ANILINE & CHEMICAL Co., Inc. Brit. 192,376, Jan. 12, 1923. Alkyl, aryl, and aralkyl derivs. of carbazole are prepd., without the intermediate formation of K carbazole, by direct treatment with the alkylating, etc., agent in presence of a dehydrating agent, such as powdered or granular caustic alkali, with or without a solvent, and at ordinary or raised temps. The solvents mentioned as suitable are solvent naphtha, chlorobenzene, toluene and steam-distd. kerosene. The app. employed may be of iron or glass and is fitted with a reflux if a solvent be used. The proportions preferred are 2.5 mol. of caustic alkali in the form of 20-mesh particles and 1 l. of solvent to 1 mol. each of carbazole and alkylating agent. The use of quicklime as a dehydrating agent for the reaction is also referred to.

Acetone. ELEKTRIZITÄTWERK LONZA. Brit. 192,392, Jan. 24, 1923. Acetone is produced by passing a mixt. of C_2H_2 and steam at a temp. of 350-450° over a catalyst comprising the hydroxide, oxide or carbonate of Th or a double salt of Th and an alkali or alk. earth metal. The catalyst is mounted on a carrier, such as burnt clay or pumice, and can be regenerated by heating in a current of air and steam. Cf. 109,983.

Saccharic and tartaric acids. L. GRAF and E. JACOBY. Can. 233,734, Aug. 21, 1923. A carbohydrate, such as starch, is mixed with water, " H_2SO_4 , concd. H_2SO_4 and HNO_3 " are added thereto with a metal catalyst, the mixt. is heated and an oxidizing agent (HNO_3) is gradually added.

Sublimation of anthracene and anthraquinone. C. R. DOWNS. U. S. 1,464,844, Aug. 14. A gaseous mixt. contg. anthracene and anthraquinone is maintained for a considerable time at a temp. of about 200° in order to obtain anthraquinone crystals.

Metalddehyde. T. LICHTENHAHN and E. LUSCHER. Can. 233,540, Aug. 14, 1923. AcH is treated with a metal bromide, such as $CaBr_2$, which is capable of splitting off HBr.

11—BIOLOGICAL CHEMISTRY

PAUL E. HOWE

A—GENERAL

FRANK P. UNDERHILL

The occurrence of zinc in oils from animals and plants. L. K. WOLFF. *Nederl. Tijdschr. Geneeskunde* 67, II, 399-400(1923).—*Cod-liver oil*, ashed in an elec. furnace, yields no Zn. If it is burned, by heating with HNO_3 and H_2SO_4 23-40 mg. per kg. is found. *Egg white*, treated in the same way, proves free from Zn; the *yolk* contains 4 mg. per l.; *coconut oil* contains 12.5-40 mg. No relation between vitamins and Zn content can be found.

R. BEUTNER

J. P. Langlois. J. E. ABELOUS. *Rev. gén. sci.* 34, 421-5(1923).—An obituary, with portrait.
E. J. C.

Superficial tension, swelling and narcosis. W. KOPACZEWSKI. *Compt. rend.* **176**, 1576-9(1923); cf. *C. A.* **16**, 1811.—Strips of gelatin were placed in different solns. for 2 hrs. at 37° and the amt. of swelling observed. There was an absence of parallelism between the superficial tension of the narcotic substances and the degree of swelling of the gelatin. Salts of Mg increase the swelling of the gelatin. It is not possible to draw conclusions as to the action upon the gels of the nerve cylinder by narcotic substances, and the swelling of colloidal gels in itself does not explain the mechanism of narcosis.

L. W. RIGGS

Is pyruvic acid a step in the decomposition of glucose in the course of glucolysis? L.-J. SIMON AND E. AUBEL. *Compt. rend.* **176**, 1925-7(1923).—In a series of beakers is placed a soln. of Na pyruvate 20 cc., physiol. serum 20 cc., total blood made uncoagulable by $(\text{NH}_4)_2\text{C}_2\text{O}_4$ 10 cc. The mixt. is allowed to stand at 37° for variable lengths of time and the content of pyruvic acid detd. For this purpose 10 cc. of water is added to the mixt. and 10 cc. of a 20% soln. of CCl_3COOH , the ppt. is filtered out and from 35 cc. of the filtrate a phenylhydrazone is made, sepd. and titrated with KOH. After 24 hrs. contact in the original mixt. about 7% of the pyruvic acid has disappeared, which is no more than would disappear from a soln. of Na pyruvate. This amt. is not comparable with a 80% disappearance of glucose under similar conditions. Normal horse or dog blood contains no pyruvic acid. Citrated normal blood was allowed to stand under toluene for 6 hrs. at 37° when no pyruvic acid was found. Pyruvic acid is not to be considered as an intermediate product in the decompn. of glucose.

L. W. RIGGS

Physico-chemical basis of psychic phenomena. ALEXANDER FORBES. *Science* **58**, 49-50(1923).—Favorable comment is made on a paper of the above title, by Hughes and King (*C. A.* **17**, 2429), also on other recent work in the field of nerve impulse and conductivity.

L. W. RIGGS

Investigation of gastric juice as to its activity in dissolving protein. ERNST KUEHLWISER AND OTTO RÖSLER. *Biochem. Z.* **136**, 38-48(1923).—When "quantity of protein dissolved in 14 hrs." is plotted against "concn. of a pepsin prepn. or of gastric juice," the curves are almost exactly superimposable if dilns. of the enzyme are adjusted properly. The prepn. of such curves should afford a superior method of comparing enzymic activities.

GEORGE ERIC SIMPSON

The caseolytic action of intestinal juice and its general distribution in the tissues of animal organisms. ANTONINO CLEMENTI. *Biochem. Z.* **136**, 71-7(1923).—Digestion of casein by intestinal juice is not due to a sp. enzyme, but to a generally distributed crepsin. It occurs in exts. of all mammalian tissues examd. Tissues from other vertebrates exhibit caseolytic action in amphoteric, or slightly alk. reaction, but not in 2% NaOH. The intestinal juice and the ext. of the intestinal mucosa of the dog digest casein and protamine, but not other proteins (egg-albumin, zein, etc.). Unboiled fibrin is digested by reason of preliminary autolysis.

GEORGE ERIC SIMPSON

Blood gas analyses. XIII. The influence of α -rays on hemoglobin and blood corpuscles. H. STRAUB AND KL. GÖLLWITZER-MEIER. *Biochem. Z.* **136**, 128-39(1923); cf. *C. A.* **17**, 2590.—Irregularities occur in the curve which results when CO_2 -tension is plotted against the CO_2 -combining power of hemoglobin solns., or of suspensions of red blood cells in physiol. NaCl. These are not found after intensive irradiation. The elec. double-layer at the phase boundaries is now lacking, and the law of mass action holds.

GEORGE ERIC SIMPSON

The nomenclature of the proteases. CARL OPPENHEIMER. *Biochem. Z.* **136**, 140-1(1923); cf. *C. A.* **17**, 1033.—The name peptase is confusing and should be discarded. The following nomenclature is proposed provisionally. If found acceptable, it will be used in the forthcoming edition of the *Handbuch d. Biochemie. A. True proteases.* (These split proteins to peptides. They do not attack peptides.) 1. *Pepsinases* (optimum in acid reaction). 2. *Tryptases* (optimum about neutral, pH 6-8); *B. Peptidases* or *creptases*. (These do not attack proteins, but split peptides or peptones.)

GEORGE ERIC SIMPSON

The constituent of urine described under the name "Oxyproteic acid." E. FREUND AND ANNA SITTENBERGER-KRAFT. *Biochem. Z.* **136**, 145-53(1923).—A non-colloidal oxyproteic acid, $\text{C}_{10}\text{H}_{17}\text{O}_{12}\text{N}_3$, which gives no protein reactions and yields on hydrolysis urica and a N-contg. org. acid, m. 260°, was prepd. The method of prepn. is described in detail.

GEORGE ERIC SIMPSON

New dielectric constants. RUDOLF KELLER. *Biochem. Z.* **136**, 163-8(1923); cf. *C. A.* **15**, 2104.—The dielec. consts. of a variety of substances of biochem. interest are detd. In spite of a large content of substances with a low const., nerve, cut lengthwise, has a high const. It evidently contains a substance with an unusually high dielec. const.

GEORGE ERIC SIMPSON

Chlorinated proteins. E. SALKOWSKI. *Biochem. Z.* 136, 169-89(1923).—The chlorinated proteins were prepd. by dissolving 5 g. protein and 5 g. NaClO₂ in 125 cc. of H₂O each, mixing and heating with 20 cc. concd. HCl. The *chloroalbumose*, pptd. with AmSO₄ or phosphotungstic acid, and dehydrated by treating with alc. and ether, contains 5.57% Cl. It retains albumose characteristics, except that reactions dependent on cyclic or heterocyclic rings are practically lacking. *Chlorocasein*, pptd., after treatment with NaOH, by HCl, and dehydrated with alc. and ether, contains a little phenylalanine. Otherwise cyclic and heterocyclic rings are absent. It is resistant to bacterial decompn., which produces no indole.

GEORGE ERIC SIMPSON

The effect of organ extracts on blood catalase. O. STEPPUHN AND A. TIMOREJIVIA. *Biochem. Z.* 136, 213-23(1923).—The sterile ext. of various organs has an accelerating effect on blood catalase which is independent of C₁₂ or salt content. The actual catalase content of the different tissues is proportional to this accelerating action. It follows that the catalase content of all organs must lie at about the same level and is really the effect of differences in the amt. of activator.

GEORGE ERIC SIMPSON

The autoclave hydrolysis of proteins with the aid of carbonic acid and oxalic acid. V. S. SADIKOV. *Biochem. Z.* 136, 238-40(1923).—In the autoclave hydrolysis of proteins, using H₂CO₂ (CO₂ under pressure), or oxalic acid as catalyst, an abiuuret product contg. no amino acids was produced.

GEORGE ERIC SIMPSON

Products of catalytic splitting of proteins. V. S. SADIKOV AND N. D. ZELINSKŪ. *Biochem. Z.* 136, 241-9(1923).—By hydrolysis of goose feathers with 1% HCl for 6 hrs. at 180° an abiuuret product was formed. Successive extn. with Et₂O, EtOAc, CHCl₃, and C₂H₅OH led to the isolation of a relatively small amt. of amino acids but large amts. of anhydrides from which the former are produced by splitting. A large variety of other products was isolated. Details of procedure are not given. "The constitution of the protein mol. is not that of a polypeptide, as E. Fischer proposed, but we are dealing with a system of rings among which the peptine rings occupy a dominant position. These are held together by long CH₂ chains. These systems we propose to designate *polypeptines*. The H of the —CH₂— groups may be substituted by OH or NH₂ or by a peptine or polypeptine rest." Cyclic and heterocyclic rings may be attached

to the side chain. The *peptine ring* is $\text{CH} - \text{NH} - \text{CO} - \text{CH} - \text{NHCO}$.

GEORGE ERIC SIMPSON

The anticatalytic action of hydrocyanic acid. O. WARBURG. *Biochem. Z.* 136, 266-77(1923).—This is a presentation of the data on which results already published (C. A. 17, 1804) are based.

GEORGE ERIC SIMPSON

The reversibility of fibrin coagulation. GEORG BARKAN. *Biochem. Z.* 136, 411-27(1923).—Hekma's belief that fibrin dissolved in NaOH is identical with fibrinogen is unfounded and proof of the reversibility of fibrin coagulation is therefore still lacking (cf. C. A. 10, 2762). Fibrin dissolved in 0.1 N NaOH shows the reactions of a meta-protein. While such solns. (after neutralization with HCl and re-soln. on adding a few drops of NaOH) can be pptd. with serum; egg albumin treated thus acts similarly. A clear soln. of fibrin in 0.02% NaOH is not pptd. by neutralization or by protein-free thrombin solns. It is pptd. by serum and by 0.06% (or stronger) NaCl. Pptn. by serum is thus due to its salt content.

GEORGE ERIC SIMPSON

Studies on the influence of glycine on the enzyme action of a soy-urease preparation. I. **The relation between urea concentration and urease action and the influence of glycine on the same.** NAOSABURO KATO. *Biochem. Z.* 136, 498-529(1923); cf. C. A. 17, 2719. —In a urease prepn. 2 components are found: (1) the enzyme itself and (2) an unknown substance, X. In urease activity 2 reactions are involved: (a) the formation of urea-X and (b) the breaking down of urea-X to form CO₂ and H₂O. Glycine may replace X under certain conditions. These generalizations are in part based on the following observations: (1) The favorable effect of glycine on urease reaches its max. only after some time. (2) The degree of this favorable effect depends on the time of adding the glycine, i. e., when time is allowed for urea and glycine to combine, urease activity is favored. (3) By treating a urease prepn. with freshly pptd. neutral Ca phosphate 2 fractions result. Combined, they have the same activity as the original prepn.; each has little activity in itself. The action of 1 fraction is increased by adding glycine or the other fraction. (4) Although urease kept on ice loses its activity, nevertheless the inactive soln. exerts a favorable influence on fresh urease, which is then no further favored by glycine. In expts. on comparative urease activity under different conditions it is necessary to try the same urease on a series of urea solns. of different concn. For any urease prepn. for a definite amt. of urease there is a definite urea concn.

for optimum activity. ("Equivalent urea concn.") The detn. of this const. (1) and of 3 other const. is necessary in any qual. detn. of urease activity; (2) the amt. of NH_3 formed at this optimum; (3) the relation: amt. of NH_3 formed at any urea concn./the amt. of NH_3 formed at optimum urea concn. (the "gradation"); and (4) the amt. of favorable action on adding glycine when the urea concn. is less than the optimum. Some factors affecting these const. are detd. The data are extensive. G. E. S.

The salt hydrolysis of starches. II. W. BIEDERMANN. *Biochem. Z.* 137, 35-52 (1923).—A general discussion based on results previously reported. See C. A. 14, 1345; 15, 3647; 17, 2653; 16, 2520. GEORGE ERIC SIMPSON

Preparation of melanin from benzene. OSCAR ADLER. *Biochem. Z.* 137, 201-5 (1923); cf. C. A. 17, 731.—A non-nitrogenous melaninic acid is prepd. from benzene according to the previously described method (C. A. 16, 2928). From this an anhydride, a melanin, is prepd. from which, on hydrolysis, the acid is again produced. The properties of these preps. agree well with those from natural sources. G. E. S.

Studies on urease. II. STURE LÖVGREN. *Biochem. Z.* 137, 206-57(1923); cf. C. A. 15, 3291.—The equation: p_H optimum = $-0.1 \ln a + 7.25$ expresses the relation between the shifting of p_H optimum and urea concn. It is examd. experimentally for urea concns. up to 0.8 M and phosphate concns. of 0.1 to 0.5 M. The point of optimum p_H is independent of enzyme and phosphate concn. and reaction time. The equation: $K = (a/E.t) \ln(a/(a-x))$ holds for the initial stages of urease activity and av. urea concns. It is not independent of time. A somewhat empirical, more generally applicable, but involved, equation is tentatively proposed and examd. experimentally. "It affords little insight into the mechanism of urease activity. It is of practical use in providing the possibility for the calcn. of enzyme activity from the NH_3 produced in Folin's procedure, and thus permitting comparison of 2 preps., even when reaction time, urea concn. and buffer concn. vary." G. E. S.

The ability of proteins to unite with dyes. KOJIRO UMETSU. *Biochem. Z.* 137, 258-72(1923).—When basic dyes are added to casein solns. the isoelec. point is shifted to a position of greater C_H . Acid dyes have the opposite effect. The different basic or acid dyes compared *inter se* shift the isoelec. point each in a sp. unpredictable degree. The union between protein and dye is not chiefly governed by the possession of opposite charges. This factor det. salt formation (ionized or unionized). The actual union is analogous to an unionized salt, the formation of which depends on the sp. affinity of oppositely charged ions. GEORGE ERIC SIMPSON

Mechanism of cell oxidations and the effect of hydrocyanic acid. WERNER LIPSCHITZ. *Arch. ges. Physiol.* (Pflüger's) 196, 463-502(1922).—The biological reduction of the colorless *m*-dinitrobenzene to the yellow *m*-nitrophenylhydroxylamine, with a colorimeter to detect the change, serves as a quant. method for measuring respiratory and fermentative changes in tissues. With minced frog muscle (2 g. of tissue in 10 cc. of distd. water) 15 to 25 mg. of the reduction product is obtained in 8 hrs. With the tissue suspended in NaCl or KCl solns. the reduction is intensified; suspended in CaCl_2 (in the concn. present in Ringer soln.) reduction is diminished. Distd. water is a more favorable medium for the process than is the bicarbonate-contg. Ringer soln. A phosphate mixt., with a p_H of 7.4, is the best medium, yielding in 2 hrs. about 20 mg., in 4 to 8 hrs. 30 to 40 mg., and in 8 to 24 hrs. up to 50 mg. of the reduction product. Under anaerobic conditions the metabolism involves the production of CO_2 , the amt. yielded by 2 g. of tissue in distd. water being 0.6 mg.; in the optimum medium 1.3 mg. These findings, compared with the respiratory quotient of 1.06 (Meyerhof), suggest that in the presence of nitrobenzene more than 80% of the lactic acid present is incompletely oxidized. This may perhaps be ascribed to a fixation of the intermediary metabolic products, such as acetaldehyde, by the nitrophenylhydroxylamine. Very low concns. of HCN exert an inhibitory effect upon the nitro reduction, but the inhibition in contrast with the respiration inhibition and in contrast with the action of narcotics, is never complete, for with 0.5% present the nitro reduction reaches 4 to 9 mg. With frog muscle in which the structure has been destroyed the reduction is favored by HCN, as is the case also for muscle and fumaric acid. The reduction in the presence of HCN is a thermolabile process, associated with the presence of a coenzyme. It may be that in the presence of HCN the respiration-like oxidation-reduction processes are dispensed with in favor of processes of fermentative nature. G. H. S.

Action of ultra-violet light upon protein solutions. I. RUDOLF MOND. *Arch. ges. Physiol.* (Pflüger's) 196, 540-59(1922).—Globulin and solns. of fibrinogen show increased stability of colloidal condition when treated with ultra-violet light, as is manifested by an increase in the temp. of coagulation, and a broadening in the coagulation zone. The reactions of the solns. toward $(\text{NH}_4)_2\text{SO}_4$ and alc. are but slightly, if

error due to non-amino compds. The initial gas vols. are corrected for the N from the slowly reacting amines by the somewhat lengthy time-factor method of Levene and Van Slyke. With blood filtrates no difference was found in the amino acid N value of a 5% $\text{CCl}_3\text{CO}_2\text{H}$ filtrate when the acid was destroyed by boiling with or without previous diln. with H_2O . The av. amt. of amino acid N found in bloods analyzed by this procedure was about 5 mg. per 100 cc.; the highest figures, 7-9 mg., were obtained in cases of nephritis and conditions associated with circulatory disturbances. II. **The diamino nitrogen in the protein-free blood filtrate.** *Ibid* 867-71.—The method is an adaptation of the Hausmann procedure. Ppt. 25-40 cc. of blood by the heat- $\text{CCl}_3\text{CO}_2\text{H}$ method of Bock. Boil the filtrate slowly for the removal of the excess of $\text{CCl}_3\text{CO}_2\text{H}$. Acidify the soln. with 2 cc. of concd. HCl and dil. to 40 cc. in a graduated cylinder. Neutralize 20 cc. and boil down to small vol. for the estn. of the total free amino acid N. Treat 20 cc. with 5 cc. of phosphotungstic acid reagent and allow to stand for 48 hrs. at room temp. Filter, make an aliquot (usually 20 cc.) of the filtrate slightly alk. to phenolphthalein, then just acid with AcOH and conc. to small vol. for analysis in the Van Slyke app. The difference between the 2 values, properly corrected for blanks, gives the amt. of diamino N in the blood filtrate. Values ranging from 0.13 to 4.54 mg. per 100 cc. of blood were found, constituting from 20 to 60% of the total free amino acid N. No const. relationship was found between the values for total and diamino acid N, and a high total value is not always accompanied by an increased diamino N. III. **A study of the occurrence of peptide nitrogen in the blood.** *Ibid* 873-9.—The presence of peptide N in amts. greater than 1 mg. per 100 cc. (the probable limit of the explt. error) was demonstrated in 30 samples of pathol. bloods. "No significant quantities of peptide N were found in 3 normal human bloods and 5 samples of fresh defibrinated beef blood. The amt. of peptide N found in the bloods from hospital patients is by far too small to account for the undetd. N of pathol. bloods with a high non-protein N. It would probably not fully account for the unknown N of bloods with a total non-protein N falling within the normal limits, only perhaps in exceptional cases." The max. amt. of peptide N found was 7.91 mg. in a case of hypertension. The estn. of peptide N depended on the detn. of the amino acid N by the Van Slyke method before and after hydrolysis of the mixed amino acid and peptide soln. A. P. LOTHROP

The preparation of creatinine from creatine. GRAHAM EDGAR AND W. S. HINGGARDNER. *J. Biol. Chem.* 56, 881-6(1923).—The methods involve the conversion of creatine into creatinine-HCl and the formation of creatinine from the hydrochloride by treatment with NH_4OH . Several procedures are described but the following gives a product which is practically 100% pure and which, although not intended for use as an analytical standard, gave results in the authors' experience undistinguishable from those obtained with samples prepd. especially for this purpose. Place 100 g. of com. creatine, previously dried at 100° to remove H_2O of crystn., in a closed flask connected to an automatic HCl generator (a Kipp filled with fused NH_4Cl and H_2SO_4). Disconnect the flask 2-3 times a day so as to break up the caked mass with a glass rod. The reaction is complete in about 48 hrs. Dry the moist mass for a short time at 100° . Dissolve the solid creatinine-HCl in 0.8 of its wt. of H_2O , warming to effect soln., and pass NH_3 gas rapidly into the soln., keeping the mixt. cooled in ice. Stop the current of gas when the ice-cold mixt. gives a strong odor of NH_3 . Allow to stand for an hr. or so, filter off the creatinine with suction, wash with a little ice-cold concd. NH_4OH and finally with alc. Dry at 100° . The color may be removed entirely by decolorizing the hydrochloride with charcoal but the yield is materially lowered thereby. Creatinine can be satisfactorily recrystd. as follows: Dissolve 1 part by wt. in 5 parts of H_2O , previously heated to 65° , as rapidly as possible. Add 2 vols. of Me_2CO at once and cool the mixt. in ice. After standing a few hrs. filter off the creatinine, wash with Me_2CO and dry. About 65% is recovered. The method is equally applicable to treatment of mixts. of creatine and creatinine or to the repurification of creatinine. A. P. L.

Dye-protein aggregates. I. Congo fibrin. I. P. SHACKELL. *J. Biol. Chem.* 56, 887-94(1923).—An apparently homogeneous prepn. of stained fibrin can be prepd. in the following manner: Dissolve 50 g. of well washed and finely hashed fibrin from which the excess of H_2O has been squeezed out in 500 cc. of hot 0.1 N NaOH. Filter through glass wool and dissolve 5 g. of Congo red in the filtrate. Ppt. the dye and protein together by adding N H_2SO_4 . Wash the Congo fibrin with distd. H_2O 3 times by decantation. Suspend the prepn. in 500 cc. of satd. NaCl soln. and boil with const. stirring for 30 min. to render the material as insol. as possible. Filter through a Buchner funnel and wash repeatedly with large vols. of boiling distd. H_2O until no further color is removed. Dry the Congo fibrin *in vacuo* over H_2SO_4 , pulverize and pass through a 100 mesh sieve. A suspension of the product in glycerol has yielded no color to the

glycerol in 2 years and a suspension in distd. H_2O may be kept at 10° for a month without yielding up any color. A slight loss of color occurs in 0.5% Na_2CO_3 in a few hrs. but no color is given in 0.1 N HCl until after several days. A simpler method of prep. dyed albumin is as follows: Strain white of egg through cheesecloth, then dil. with 4 vols. of 5% $NaCl$ and filter through cotton- or glass-wool. Add an excess of the dye, previously brought into soln. Heat in a boiling water bath with frequent stirring. Filter the coagulated protein on a Buchner funnel and wash with boiling distd. H_2O until the filtrate is colorless. The washing process is very tedious; a mass of moist dyed protein of about 40 g. requires 50-100 washings of 200 cc. each. Preserve the material in glycerol or dry *in vacuo*. "Results of peptic digestion of Congo fibrin suspensions show that the progress of digestion is largely dependent upon the size of the particles of substrate. Peptic digestion of the Congo fibrin can be followed accurately with quantities weighing less than 10 mg. and in a concn. of the substrate such that the products of digestion can exert no appreciable effect upon the reaction. It is questionable whether mass law concepts can be applied to the description of the digestion of fine suspensions of Congo fibrin by pepsin. Work still in progress is concerned with the prepn. and standardization of dyed proteins suitable for precise measurements of peptic activity." A. P. LOTNORF.

The acetonitrile test for thyroid and of some alterations of metabolism. RUD HUNT. *Am. J. Physiol.* 63, 257-99 (1923).—A review of certain features of the test as applied to the thyroid with new exptl. data. The importance of diet as affecting the resistance of mice to MeCN is pointed out. It is thought that vitamins may be concerned in this action. The parallelism between I content and physiol. activity (by MeCN test) of thyroid is confirmed. The physiol. activity of thyroxin is (in terms of I content) less than that of thyroid. There is no evidence of physiol. inactive I in the thyroid. In certain pathol. cases, especially those in which the thyroid is involved, but also in nephritis, the blood contains unknown or unidentified substances which markedly increase the resistance of mice to MeCN. These substances apparently are not among those ordinarily detd. in chem. blood analysis. J. F. LYMAN.

A simple method for the determination of carbon in aqueous liquids. E. FREUND AND G. BORSIBER. *Biochem. Z.* 136, 142-4 (1923).—A preliminary investigation into the development of a short method for C detn. based on the Messinger procedure.

GEORGE ERIC SIMPSON

Can peptones be used to prevent coagulation of blood in investigations of the gaseous exchange? G. KELEMEN. *Biochem. Z.* 136, 154-8 (1923).—Peptones in doses sufficient to prevent coagulation markedly influence gaseous exchange. G. E. S.

Method for the quantitative determination of yeast glycogen and the question of the action of alkali on glycogen formation in yeast. PAUL MAYER. *Biochem. Z.* 136, 487-97 (1923).—The method of Pflüger for glycogen estn. gives too high results with yeast. Yeast gum comprises as much as 50% of the ppt. obtained. This must be removed by pptg. the glycogen with satd. $(NH_4)_2SO_4$. The glycogen of yeast is not altered by incubation in 0.16 M $KHCO_3$ or in Karlsbad H_2O . Elias and Weiss' expts. were repeated (cf. *C. A.* 17, 1603) and could not be confirmed. No increased glycogen formation was produced by incubating yeast in dil. alk. The discrepancy is not due to the failure of E. and W. to get rid of the yeast gum. GEORGE ERIC SIMPSON.

Drying and weighing in micro-analysis. A. V. SZENT-GYÖRGYI. *Biochem. Z.* 136, 102-6 (1923).—The Pregl asbestos filter and weighing tube is modified slightly to prevent inhibition of H_2O by hygroscopic substances. This arrangement also permits drying *in vacuo*. For drying at high temps. a special drying chamber is described. G. E. S.

The gravimetric micro-determination of cholesterol. A. V. SZENT-GYÖRGYI. *Biochem. Z.* 136, 107-11 (1923).—The cholesterol from 1 cc. blood (not over 4.5 mg.) is dissolved by warming in 2 cc. Me_2CO in a micro-beaker, 1 cc. digitonin soln. (1 g. in 50 cc. 80% $EtOH$) is added, about $1/2$ the liquid is evapd. on the H_2O bath, and the beaker cooled by standing $1/4$ hr. at room temp. The ppt. is washed into the modified funnel (cf. preceding abstr.) with H_2O . It is then washed twice with Me_2CO , twice with Et_2O , 3 times with warm $CHCl_3$, once with Et_2O , once with Me_2CO , and 5 times with hot H_2O . About 1.5 cc. of liquid is used for each washing. Washing with H_2O is continued until the small bubbles at the lower end of the funnel tube show that digitonin is practically absent. The tube may be dried in the special chamber, and weighed. Wt. of ppt. $\times 0.25$ = cholesterol. The error is less than 1.5% when this factor is used. The original is to be consulted for details of technic. G. E. S.

The titrimetric micro-determination of cholesterol. A. V. SZENT-GYÖRGYI. *Biochem. Z.* 136, 112-8 (1923).—The procedure is the same as that for the gravimetric estn. (cf. preceding abstr.) to the washing of the ppt. with H_2O . It is washed 3 times with cold

H₂O, the ppt. being rinsed into the narrow part of the funnel. Steam is now passed through a glass mantle with which the funnel is fitted for this estn., and the washing continued to remove digonin. The collecting flask is replaced by a 200-300 cc. flask. Exactly 5 cc. of K₂Cr₂O₇ soln. (10 g. K₂Cr₂O₇ in 1 l. concd. H₂SO₄) is poured on to the filter, the narrow filter tube being kept full of the soln. This is continued, with addn. of new pipet-fulls, until the ppt. is completely oxidized. The filter is rinsed into the flask with a little H₂O. If the liquid in the flask is brownish or pure blue, another pipet-full of K₂Cr₂O₇ soln., is added so that an excess is surely present. This is allowed to stand 1/4 hr. An equal vol. of H₂O and 10 cc. 5% KI are added and the mixt. is titrated with 0.1 N Na₂S₂O₄, with 5 drops of 1% starch soln. for each 50 cc. of H₂O used. 8.6 cc. 0.1 N K₂Cr₂O₇ or Na₂S₂O₄ = 1 mg. cholesterol. This method is as accurate as the above gravimetric method. G. E. S.

A method for the determination of urea based on the hypobromite reaction. B. M. MARGOSCHES AND HEINRICH ROSE. *Biochem. Z.* 136, 119-27(1923).—Solns. required: (a) To 8 g. NaOH in 1 l. H₂O is added, with cooling, 8 g. Br; (b) 0.1 N HCl; (c) 0.1 N NaOH. To a weighed amt. of the substance whose urea or NH₃ content is to be detd. is added 10 cc. of a. After heating 3 mins., 0.2-0.3 g. NaBr is added, and 500 cc. of b. The excess Br is boiled off. After cooling, the excess acid is titrated with c. A blank is always necessary. After subtracting the blank titration, the amt. of NH₃ or urea is calcd. from the equations: 2NH₃ + 6NaOH + 3Br₂ = 6NaBr + 6H₂O + N₂, and CO(NH₂)₂ + 6NaOH + 3Br₂ = 6NaBr + 5H₂O + CO₂ + N₂. This method may be used to check the ordinary hypobromite method. GEORGE ERIC SIMPSON

Determination of the peroxidase content of plant juices. G. DORFMÜLLER. *Z. Ver. deut. Zuckerind.* 73, 316-22(1923).—Willstätter's method (*C. A.* 13, 453; 17, 1973) requires large quantities of costly reagents. The following procedure has been found satisfactory: Two cc. of a 10% soln. of pyrogallol and a measured quantity of plant juice which, according to preliminary tests, will give the expected color, are added to 190-5 cc. water. The mixt. is brought to a temp. of 20-20.5° and then 1.5-2 cc. of a 1% soln. of H₂O₂ are added. After exactly 5 min., 10 cc. of the test soln., from which no purpurogallin must have pptd., are poured into a high test-tube with ground-glass stopper, which already contains 2 drops dil. H₂SO₄. The test-tube has the same dimensions as those of the sealed tubes of the Silber colorimeter (*C. A.* 8, 768). The 10 cc. of the soln. are extd. with 15 cc. Et₂O, and the color of the supernatant Et₂O is compared with the NH₄ picrate standards of Silber. The standards for 0.04 and 0.15 mg. N₂O₄ are the most suitable. In case of weak enzyme preps. a greater vol. of them is used and that of the water diminished so as to have a total vol. of 200-5 cc. Small variations in the latter do not affect the results. The amts. of Et₂O evapg. during the test are always about the same, and it is not necessary to complete again to a certain vol. The accuracy of the method first increases with increasing diln., and then decreases again. Very active peroxidase preps. must first be dild. Under proper conditions the accuracy of the method is = 10%; at great diln. it may reach 15% and even 20%. The presence of chlorophyll, and also that of catalase interfere to some extent. F. W. ZERBAN

Arginase. VI. Modification of the volumetric method for detecting arginase. ANTONINO CLEMENTI. *Atti accad. Lincei* [v] 31, ii, 454-9(1922); cf. *C. A.* 13, 1600.—If the acid liquid obtained by the acid hydrolysis of edestin, or the phosphotungstic acid ppt. of hexone bases obtained therefrom, is treated *in vitro* in presence of toluene with the pulped liver of a mammifer (monkey, man, rat) which contains arginase, a considerable increase is effected in the proportion of N titratable with formaldehyde. No such increase occurs, however, if the above liver is first boiled or if hen's liver, which is devoid of arginase, is used. Conclusion: The increase in N titratable with formaldehyde corresponds with the ornithine formed by scission of the arginine by the arginase, and such increase furnishes an indication of the presence of arginase in an organ or in an org. liquid. J. C. S.

C—BACTERIOLOGY

A. K. BALLS

Formation of phenol by intestinal bacteria. L. R. J. BOUWMAN. *Pharm. Weekblad* 60, 845-7(1923).—Out of 32 samples of feces examd. 7 contained phenol-forming bacteria. The pure cultures isolated all belonged to the coli group. They behaved like coli bacilli in their growth upon agar, potato and gelatin (without liquefaction), acid formation on litmus-whey, and curdling of milk. All but 2 formed acid from sucrose. 9 of the 19 cultures developed red colonies with a metallic luster, though the

color in some cases was not uniform. Those with uniform red color did not form indole, in contrast to the mutating cultures, which readily formed indole. A. W. DOX

The fermentation of pyruvic acid in the presence of sugar. A. N. LEBEDEV AND A. N. POLONSKI. *J. Russ. Phys. Chem. Soc.* 49, 1, 328-44 (1917).—Old yeast (2 yrs.) ferments sugar vigorously but attacks pyruvic acid only very slowly. New yeast ferments both sugar and pyruvic acid vigorously. Quant. data are presented on the amts. of CO_2 , EtOH and CH_3CHO formed by the fermentation of sugar, pyruvic acid and sugar plus pyruvic acid. The fermentation of pyruvic acid produces less alc. and CO_2 than the fermentation of sugar. In the fermentation of pyruvic acid in the presence of sugar the quant. of CO_2 is increased while the amts. of CH_3CHO and EtOH are decreased. Curves show the course of the fermentation of pyruvic acid in the presence of sugar at different time intervals and at different concns. of sugar and pyruvic acid (at 25°). A quant. study of the amt. of CH_3CHO produced by the fermentation of various ratios of sugar: pyruvic acid (S:P) is carried out. 100 mg. of pyruvic acid produces as much CH_3CHO as 777.2 mg. sugar. In the presence of 100 mg. pyruvic acid the quantity of CH_3CHO is not decreased as the concn. of sugar increases. On the contrary the larger the ratio S:P, the less aldehyde is formed. The max. amt. of CH_3CHO formed by the fermentation of pyruvic acid in the presence of sugar (over a wide range of concn.) is about 10.5 mg. More CH_3CHO can be produced from glyceric acid than from pyruvic acid. GEORGE W. PUCHER

The fermentation of glyceric and pyruvic acids. A. N. LEBEDEV AND A. N. POLONSKI. *J. Russ. Phys. Chem. Soc.* 49, 1, 344-57 (1917).—The chief end products of the fermentation of glyceric acid by yeast are CO_2 and EtOH with the formation of only very small amts. of CH_3CHO . More CO_2 , EtOH, and CH_3CHO are produced from the fermentation of pyruvic acid in acid soln. than in neutral soln. Thus 0.8% pyruvic acid in acid soln. (H_2SO_4) forms as much CO_2 as 1.6% pyruvic acid in neutral soln. More acetic acid is formed in neutral than in acid soln. However, under both conditions the chief products are CO_2 and CH_3COOH . The fermentation of pyruvic acid goes through the intermediate formation of CH_3CHO , which by a Cannizaro reaction is transformed into CH_3COOH and EtOH. The EtOH is then partially oxidized to CO_2 and H_2O . Parallel expts. with glyceric acid show that this compd. followed a course similar to that of pyruvic acid. However, there seems to be a greater production of CH_3CHO with glyceric than with pyruvic acid. GEORGE W. PUCHER

D—BOTANY

B. M. DUGGAR

A study of the tolerance of plants to acid conditions as determined by the hydrogen-ion concentration. L. W. TARR. Delaware Agr. Expt. Sta., *Bull.* 133, 13-4 (1923).—Seedlings of wheat, beans and corn were grown in nutrient solns. which were maintained at const. H-ion concn. over a range from approx. p_{H} 3 to 8 at intervals of 1 p_{H} . The addn. of K H phthalate to the nutrient soln. served as a buffer. A reaction of p_{H} 3 was prohibitive to growth in all cases. Max. growth of wheat seedlings occurred at a reaction of approx. p_{H} 4; a greater concn. was harmful, and a lesser concn. exerted no harmful effects until a p_{H} value of 6 was attained. At this and at all lesser concns. chlorosis appeared in the seedlings. Max. growth of soy beans was attained at approx. p_{H} 5. The harmful effects of a reaction of p_{H} 4 were readily apparent. A lesser concn. exerted no harmful effects until a p_{H} value of 6 was attained, at which chlorosis became apparent as in the case of wheat. Max. growth with corn occurred at approx. p_{H} 5. A reaction of p_{H} 4 seemed to exert a harmful effect. Chlorosis became apparent at a reaction of a little more than p_{H} 6. Chlorosis was due to the insoly. of Fe at all H-ion concns. less than p_{H} 6. The insoly. of Fe made it unavailable to the plant and chlorosis resulted. J. J. SKINNER

Some factors affecting the rate of change of hydrogen-ion concentration in nutrient solutions. L. H. JONES. New Jersey Agr. Expt. Sta., *Ann. Rept.* 1921, 330-3.—Wheat plants were grown in Shrive's nutrient soln. to study the influence of total concn., vol. of soln., and varying number of plants upon the rate of change and H-ion concn. of the nutrient medium in contact with the roots of the growing plants. The rate of change of H-ion concn. decreased with an increase in total osmotic concn. value of the soln., when the vol. was const., and decreased with each increase in the vol. of the soln. when plants were grown in a soln. having a given osmotic concn. With each vol. of soln. and with each total osmotic concn. the rate of change of the H-ion concn. increased with each increase in the no. of plants grown in the soln. J. J. SKINNER

Effect of infinitesimal traces of chemical substances on photosynthesis. J. C.

BOSCH. *Nature* 112, 95-6(1923).—Photosynthetic activity of *Hydrilla verticillata*, measured by oxygen evolution, was stimulated 200% by 1 part HNO₃ in 2 billions, 80% by 10 parts ext. of thyroid gland in a billion and 85% by 1 part CH₂O in a billion.

H. A. SPOBNIK

Quantity of nitrogen in the underground portion of vetch (*Vicia sativa* F.). T. MIZUNO. *J. Sci. Agr. Soc. (Japan)* No. 233, 147-52(1922).—Five groups of vetch were planted with (1) no manure, (2) human manure, (3) CaH₄(PO₄)₂, (4) charcoal, (5) slaked lime. After a definite time the plants were cut 1 inch above the ground, and the weight and N contents of the cut and underground portions were detd. The results are given for cut, and underground portions of the plant in % of air-dried substance, resp.: (1) 2.2890, 1.9720; (2) 3.3110, 2.5714; (3) 2.5360, 2.078; (4) 3.6283, 1.7965; (5) 2.1839, 1.0569. The total N is therefore: (1) 1.5951, (2) 4.0271, (3) 7.0241, (4) 6.8572, (5) 2.7191. Thus in 1, 1/2 N is left in underground air; in 2, 3, 4, 5 approx. 1/8 N. Factors for the calcn. of residual N from wt. of fresh cut plants are given.

S. T.

Microscopic detection of Fe (Richter) 7.

E—NUTRITION

PHILIP B. HAWK

NORMAL

Composition and nutritive value of yeast grown in vitamin-free media. JUANITA E. DARRAH. *Am. Food J.* 17, No. 8, 19(1922).—Exptl. feeding of rats, briefly summarized, showed that yeast could be grown in vitamin-free media through an exceedingly large number of transfers and that such yeast contains protein and N bases of undoubted nutritive value. Evidence of dietetic value due to vitamin content of yeast *ipse facto* is not substantiated. There is only a slight indication of presence of vitamin B and none of vitamin B (A? Abstr.) and C in such yeast, which does not appear to be an active synthesizer of vitamins.

H. A. LEPPER

Studies in the growth and nutrition of dairy calves. VI. The addition of hay and grain to a milk ration for calves. A. C. McCANDLISH. *J. Dairy Sci.* 6, 347-72(1923); cf. C. A. 17, 1985.—Milk although an adequate food for calves for the first few weeks of life results in nutritive failure ultimately. If the milk ration be supplemented by a grain mixt. (corn, oats, bran, and oil meal) not only is growth checked, but death results more rapidly than when milk is the sole article of the diet. Alfalfa hay when added to a milk diet or to a diet of milk and grain will restore the animals to normal nutrition and permit normal growth to maturity. The injurious effect of the grains is presumably due to disturbance of the Ca-Mg balance, since grains contain more Mg than Ca and Ca must be drawn from the body's store of Ca (chiefly the bones) to take care of excess Mg. The beneficial supplementary effect of alfalfa hay is probably due in part to its vitamin content, and in part to its bulky character which keeps the digestive tract distended and thus renders proper digestion possible, and in the case of the grain and milk diets, to its Ca content which aids in the restoration of the proper Ca-Mg equilibrium of the body.

H. B. LEWIS

Vitamin B as a factor in nutrition. G. R. COWGILL. *Nation's Health* 5, 509-10, 561(1923).—A general review of the importance and function of Vitamin B in nutrition, with especial emphasis on its relation to the appetite. The absence of vitamin B from the diet might inhibit or completely check the so-called hunger contractions and thus influence appetite. Unpublished expts. of C. indicate that "while the normal motility of the stomach is affected after a time by vitamin B deficiency, this relationship is not definite enough to warrant the conclusion that disappearance of hunger contractions is the immediate cause of appetite failure, the lack of vitamin B serving as the remote cause."

H. B. LEWIS

New researches of the Boston "Nutrition Laboratory" on the metabolism of man and of animals. FRANCIS G. BENEDICT. *Bull. soc. hyg. aliment.* 11, 342-61(1923).—A review.

A. PAPIERAU-COUTURE

Factor causing the assimilation of calcium. CHAS. H. HUNT AND A. R. WINTER. *Science* 57, 717-8(1923).—Working on the assumption that most of the Ca is in a highly dispersed form in the cells of green plants, and hence better assimilated than the Ca of dry plants, it was attempted to imitate the cell content so far as dispersal of Ca was concerned, by adding CaCl₂ (2 Molar) to starch paste, then an equal vol. of Na₂PO₄ of the same strength. The final product, Ca₂(PO₄)₂, was thus left in a highly dispersed form. This starch paste was added to a ration of grain and dry timothy hay and fed

to 2 milking goats for a period of 30 days and the Ca balances for the last 26 days were detd. by periods of 7, 7 and 12 days, resp. Out of 6 complete accountings 5 gave a positive balance and the 6th gave a negative balance of 0.32 g. for 12 days. Milking goats fed on grain, hay and a mineral supplement always gave a negative Ca balance. It is suggested that while the vitamins of green plants may assist in the assimilation of Ca a part of the difference between green and dry plants is due to the phys. properties of the cell wall and cell content.

L. W. RIGGS

Vitamins. J. F. LYMAN. Ohio Agr. Col. Ext., *Bull.* 18, No. 3(1922-23).—A compilation of information on the occurrence and properties of vitamins and a consideration of the vitamin requirements of children and adults.

J. J. SKINNER

ABNORMAL

Scurvy produced by a diet complete and balanced but uniquely deprived of factor C. J. LOPEZ-LOMBA AND MMR. RANDOIN. *Compt. rend.* 176, 1573-6(1923). The diet mentioned is described in the following paper (cf. also *C. A.* 17, 2598). The exptl. animals, rabbits and guinea pigs, were brought to the new diet gradually, thus avoiding an initial loss of wt. The daily addn. of 3 cc. of citron or orange juice to the diet assured a normal growth in the young, and excellent health in the adult animals. The symptoms of avitaminosis are described, the most general being the loosening of the molars. Other symptoms are the difficulties of the capillary circulation due to alterations in the vascular endothelium, the bone marrow is congested, the bones become thinner and more fragile. The symptoms of congestion are more pronounced in young animals. In scurvy there is an increase in the wt. of the suprarenals and especially of the thyroid, little or no variation in the kidneys, spleen and testicles, but a marked loss in the wts. of the liver and thymus. Cf. following abstract.

L. W. RIGGS

Change in the weights of organs in the guinea pig during avitaminosis C. J. LOPEZ-LOMBA. *Compt. rend.* 176, 1732-5(1923); cf. preceding abstract.—Guinea pigs were fed a ration made up of cooked bean flour 84, granulated beer yeast 3, butter fat 4.5, Ca lactate 5, NaCl 1.5. This diet was deprived of factor C. Controls received the same diet with the addn. of 3 cc. of citron juice per day. The course of acute scurvy was divided into 4 periods: (1) Period of incubation, 1 to 6 days, during which time the exptl. animals exhibited no external symptoms to distinguish them from the controls, but in this period the thymus and thyroid are atrophied and the spleen and kidneys are hypertrophied. (2) This period from the 6th to the 15th day is characterized by hypertrophy of the suprarenals and kidneys, and atrophy of the thymus and thyroid. Toward the end of the period abortion occurs. (3) The 15th to 19th day period shows a min. wt. of the suprarenals. Diarrhea accompanied by a voracious appetite occurs. (4) From the 19th day onward in addn. to an accentuation of the preceding symptoms, hemorrhages occur, the wt. of the liver remains nearly const., the testicles slowly atrophy and the thyroid and suprarenals hypertrophy but by hemorrhagic infiltration.

L. W. RIGGS

Carbohydrate metabolism in avitaminosis. II. Glycogen and avitaminosis. J. A. COLLAZO. *Biochem. Z.* 136, 20-5(1923); cf. *C. A.* 17, 802.—Pigeons, chicks, guinea pigs and dogs were killed (1) after a normal diet, (2) after a period of starvation, and (3) in the hyperglucemic stage of avitaminosis. With guinea pigs, C only was lacking; with the other animals, A, B and C were lacking. In avitaminosis the tissues are practically glycogen-free. There is less glycogen in liver, muscle and the tissues generally, than is found in the starved animals. (The starvation period was usually about $\frac{1}{4}$ as long as the vitamin-free period.) "The same fundamentally pathol. change in carbohydrate metabolism was produced in all instances. The different vitamins, A, B and C, play the same physiol. role in carbohydrate metabolism in birds, rodents and carnivores." III. The influence of glucose administration, in small and large amounts, on the blood sugar in the normal, starving and avitaminosis body. *Ibid* 26-37.—In vitamin deficiency, the body differs from the normal or starved organism in its utilization of glucose. The hyperglucemia after large doses is more marked and more protracted, and glucosuria is more easily produced. The hypoglucemia after small doses is more protracted. In vitamin deficiency the physiol. blood sugar is not an effective stimulus for the glycogen-building function, hence the hyperglucemia. Administered glucose is a more effective stimulus, hence the hypoglucemia after small amts. of glucose. It follows that glucose administered as such is not identical with the glucose which results from the digestion of starch, and that in vitamin deficiency the power of glycogen formation is not totally disrupted, but rather its formation from a

definite sugar mol. Dogs were used. The glucose was administered by various channels. IV. The toxic influence, in avitaminosis, of the products of the intermediary metabolism after the administration of various sugars. *Ibid* 278-90.—The order of toxicity in vitamin deficiency is as follows: glucose, levulose, galactose > sucrose, lactose, maltose > starches. Administration of yeast with the sugars markedly diminishes their toxicity. The toxic symptoms are possibly produced by an intermediate substance in carbohydrate metabolism.

GEORGE ERIC SIMPSON

The compensatory influence of ultra-violet light in avitamin disturbances in the bone marrow. ISHIDO. *Biochem. Z.* 137, 184-92(1923).—Histological findings on normal rats, rats fed on polished rice, and on similar groups, irradiated. G. E. S.

A method of establishing diabetic patients on high calory diets with a ketogenic-antiketogenic ratio within the limits of safety. F. A. EVANS. *Am. J. Med. Sci.* 166, 106-13(1923).—Formulas are given from which diets may be constructed having the desired ketogenic-antiketogenic ratio.

G. H. S.

The use of fat in diabetes mellitus and the carbohydrate-fat ratio. W. S. LADD AND W. W. PALMER. *Am. J. Med. Sci.* 166, 157-69(1923).—The diet for diabetic patients to whom it is desired to give a max. caloric intake with a min. in the form of carbohydrate the carbohydrate-fat ratio can be calcd. from the formula fat ÷ available carbohydrate = fat ÷ 0.58 protein + carbohydrate.

G. H. S.

F—PHYSIOLOGY

ANDREW HUNTER

Foam membranes. E. BROUWER. *Nederlandsch Tijdschr. Geneeskunde* 67, II, 409-10(1923).—Apart from casein plates, fat globules and leucocytes, milk is found to contain peculiarly shaped small bodies which B. proves to be membranes, originally formed by adsorption of protein to gas bubbles and remaining in the milk after the gas bubbles have been dissolved.

R. BRUTNER

The amino acids of the blood. I. Behavior of the amino acids of the blood during digestion. S. MARINO. *Arch. farm. sper.* 36, 20-32(1923).—Defibrinated blood of the fasting dog contains 3.3-6.6 mg. of amino acids per 100 cc. During digestion of protein food the blood rarely contains less amino acids than the normal, but usually a distinct increase which may even approach twice the amt. present during fasting. The greatest increase occurs from the 4th to the 5th hr. of digestion and sometimes persists to the 6th hr., after which a decrease toward normal begins. II. The amino acids of the blood in prolonged fasting. *Ibid* 56-64.—During complete fasting prolonged until the death of the animal, an increase in the amino acid content of the blood begins after the 12th day and continues until death ensues. This increase is due to a breaking down of the tissues and to hepatic insufficiency, which becomes stabilized during prolonged fasting and allows the amino acids to accumulate in the blood.

A. W. DOX

The true acidity or alkalinity (hydrogen-ion concentration) of mixed normal human saliva as obtained from the resting mouth. H. H. BUNZELL. Colgate and Co., *Bull.* No. 1, 15 pp.(1923).—In the past the reaction of the saliva has usually been detd. with samples obtained by chewing paraffin and tested with litmus or phenolphthalein. Such detns. are not accurate, since the act of chewing changes the H-ion concn. in the direction of alky., also the changes in color of the indicators mentioned do not represent the degree of acidity or alky. of a given soln. In this study H-ion concn. was detd. by the methods of Clark. The standards used were checked by the gas-chain method using a potentiometer and galvanometer. Bromothymol blue was a satisfactory indicator. In some cases methyl red and bromocresol purple had to be used. Detns. of p_H in the saliva of 102 children 7-8 years of age, 135 medical students of both sexes, 50 male subjects 12 to 49 years of age, and 37 aged persons gave results averaging about 6.4 which is slightly acid. But 3 adults were as high as 7.1. Five children gave from 7.1 to 7.41. Saliva of children averaged slightly higher (6.63) than that of young adults (6.48) and that of aged persons (6.1). There appeared no relation between the reaction of the saliva and the condition of the teeth. No difference appeared between salivas collected in the forenoon and afternoon. Nineteen varieties are represented in the dentifrices used by the subjects of this study. No relation was found between the p_H value and any particular dentifrice.

L. W. RIGGS

Role of the spleen in nutrition. CHARLES RIBBET. *Compt. rend.* 176, 1581-3(1923).—Expts. made by feeding one series of 14 dogs from which the spleen had been removed and a second series of normal dogs proved that the spleen plays an important role in nutrition, especially in the assimilation of carbohydrates.

L. W. RIGGS

Chemical observations on the classification of the carotid glands with the adrenal

system. ZOLTÁN ASZÓDI AND LUDWIG PAUNZ. *Biochem. Z.* 136, 159-62(1923).—The carotid glands are not to be regarded as belonging to the adrenal system. No adrenaline could be extd. from them. GEORGE ERIC SIMPSON

The irregular exchange of ions between blood corpuscles and phosphate buffer mixtures of graded hydrogen-ion concentration. CHRISTIAN KRORTZ. *Biochem. Z.* 136, 250-65(1923).—Into a series of phosphate buffer solns. are measured equal amts. of blood corpuscles. After 15 mins. the solns. are centrifuged, and the p_{H} is redtd. Final p_{H} plotted against initial p_{H} gives a curve with a distinct kink. The explanation of this was given previously (*C. A.* 13, 2045). GEORGE ERIC SIMPSON

The irritability of the respiratory center in man and its chemistry. HERMANN BERNHARDT. *Biochem. Z.* 136, 78-101(1923).—The irritability of the respiratory center is measured by the quotient $(v' - v)/(l' - l)$, where v is the alveolar ventilation at CO_2 tension l , before administration of CO_2 ; v' is the ventilation at the higher CO_2 tension l' (cf. Loewey, *Pflügers Arch.* 47 (1893)). This quotient is used to measure changes in irritability brought about by factors other than changes in C_{O_2} of the blood. In pregnancy and in certain pathol. conditions, chiefly endocrine disturbances, significant variations are found. GEORGE ERIC SIMPSON

General cellular physiology. The capacity of muscle to swell and its permeability under various conditions. EMIL ABDERHALDEN AND ERNST GELLIORN. *Arch. ges. Physiol. (Pflüger's)* 196, 584-607(1922).—The frog gastrocnemius muscle was immersed in CaCl_2 solns. (0.2 to 0.4%) to which NaCl , MgCl_2 , and cane sugar were added to render the mixt. isotonic with 0.7% NaCl soln. In the CaCl_2 -cane sugar solns. the swelling of the muscle was the greatest, in the CaCl_2 - MgCl_2 solns. it was the least, while the reaction in CaCl_2 - NaCl mixt. was intermediate. In the mixt. of CaCl_2 and MgCl_2 (the Ca salt being present in low concns.) there was a significant increase in wt. The irritability of the muscle diminished most quickly in the cane sugar- CaCl_2 mixt., and most slowly in the MgCl_2 - CaCl_2 soln. By means of Ca detns. on the solns. it appeared that in the presence of cane sugar the muscle absorbed Ca more rapidly than in the other two solns. If KCl is added to the NaCl - CaCl_2 soln. the irritability of the muscle is reduced but the ability of the tissue to absorb Ca is unchanged. The increased permeability of the muscle when in contact with cane sugar is referable to changes in the colloidal condition of the superficial layers of the tissue, which are responsible for the union with the Ca . G. H. S.

Is the rest-current produced by salts a Beutner oil-chain current? HUGO NATANSEN. *Arch. ges. Physiol. (Pflüger's)* 196, 637-42(1922).—By measuring the potentials of a two-phase fluid chain in which oil served as the second phase it appeared that org. salts developed greater surface potentials than did inorganic salts. The action of organic salts on the rest current of muscle is consequently very weak. The rest current of muscle cannot be considered as analogous to an oil-chain current. G. H. S.

Properties of heart muscle preparations (Loewe) under various conditions. II. The influence of *l*-, *d*-, and *dl*-adrenaline on the active and inactive preparation of heart muscle. EMIL ABDERHALDEN AND ERNST GELLIORN. *Arch. ges. Physiol. (Pflüger's)* 196, 608-28(1922).—Upon the active frog heart prepn. the threshold concns. of the different adrenaline prepn. were as follows: *l*-adrenaline, 1:15,000,000; *dl* adrenaline, 1:7,500,000; and *d*-adrenaline, 1:1,500,000. With threshold doses, or concns. but slightly higher, the action of adrenaline is very transitory, but with higher concns. the action becomes more pronounced, and an after-effect becomes manifest. This latter is more evident with *l*-adrenaline than with *d*-adrenaline. In high concns. both *l*- and *d*-adrenaline not only increase the size of the contractions but diminish their frequency, an effect which may be abolished by atropine. Adrenaline of any of the 3 types may cause an irregularly beating heart to become more regular in its action. With an inactive heart prepn. a higher concn. of adrenaline is necessary to start it beating than is required to give an adrenaline effect upon an active heart prepn. Mechanical tension applied to the inactive heart reduces the amt. of adrenaline required to start the beating, but in this respect BaCl_2 is more effective. G. H. S.

Blood of domestic animals examined by new methods. III. Differential counts of the lymphocytes and monocytes in the bloods of horses, cattle, and dogs. HERMANN HERRL. *Arch. ges. Physiol. (Pflüger's)* 196, 560-70(1922).—The total leucocyte counts were, horse, 9750; cow, 8140; dog, 10610 per mm^3 . The results of the differential counts made by the Pappenheim method and by the indophenol-blue method were essentially the same. The significant figures were those secured for the lymphocytes, which were, for the horse, 33%, for the cow, 50%, and for the dog, 23%. G. H. S.

Role of the liver in the removal of hemoglobin from the blood stream. S. M.

ROSENTHAL. *J. Pharmacol.* 21, 367-76(1923).—The disappearance of hemoglobin from the blood serum following its injection intravenously has been studied in 12 normal rabbits. In a dosage of 22 to 60 mg. per kg. body wt. there was practically complete removal in 4 hrs. Ligation of the main liver, comprising 78.8% of the total liver substance, caused a marked delay in this rate of departure of hemoglobin from the blood. In 5 rabbits with the main liver ligated, an av. of 43% of the amt. injected was present in the serum 4 hrs. after injection. C. J. WEST

G—PATHOLOGY

H. GIDEON WELLS

The preparation of an exceptional hemolytic anti-dog-serum. LUIGI SANI. *Pathologica* 14, 113-6; *Chem. Zentr.* 1922, III, 301.—Contrary to Frouin, no antigens for the production of hemolytic sera in rabbits against the blood corpuscles of dogs, fowl or horses could be obtained from egg yolk, white of egg or sheep blood corpuscles washed with acetone. C. C. DAVIS

Pulmonary lipases. Their role in tuberculosis. Specific therapy for tuberculosis. R. BOSSAN. *Scalpel* 75, 273-8; *Chem. Zentr.* 1922, III, 743.—The action of pulmonary lipase is described. It is derived apparently from a cell of lymphoid character occurring in the lung. In isolated pulmonary tuberculosis caused experimentally in rabbits the lipase action steadily decreases. Through soln. of tubercle bacilli in neutral oil and filtration through Chamberland candles a vaccine was prepd. which increased the pulmonary lipase. This vaccine had a powerful action on the bacilli. C. C. DAVIS

Experimental scurvy. II. Influence of intestinal constipation on the development of scurvy. DOMENICO LIOTTA. *Arch. farm. sper.* 36, 1-5(1923); cf. *C. A.* 17, 2597.—In exptl. scurvy of the guinea pig induced by gradual habituation to an exclusive diet of rice, constipation is not as important a factor as has been claimed by others. Neither in the control animals nor in those subjected to systematic purgation by phenolphthalein did the autopsy reveal a cecum abnormally distended with feces. The final death of the animals cannot be attributed to constipation. Examn. of the lesions showed them to be characteristic of scurvy. A. W. DOW

The meaning of the speed of sedimentation of the erythrocytes for the diagnosis of carcinoma and for the establishing of freedom from recurrence after operative treatment. O GRACERT. *Arch. Gynäkol.* 118, 421-35(1923).—The speed of sedimentation of the red blood corpuscles was studied in 70 cases of operable and inoperable carcinoma of the female genital organs, before and after operation or treatment. There was always an increased speed of sedimentation in malignant disease. The acceleration in sedimentation did not run parallel with the extension of the carcinoma but was apparently dependent on the toxic effect of the carcinoma on the system. Cachexia and anemia are among the causative factors. The speed of sedimentation tended to become normal in a year after successful operation. A persisting high speed of sedimentation indicates a recurrence of the carcinoma. The method is of value in the diagnosis of cases of doubtful carcinoma of the uterus, if used in combination with other blood tests. HARRIET F. HOLMES

Neutralization of placenta toxin through serum. ISEI OBATA. *Arch. Gynäkol.* 118, 586-624(1923).—See *C. A.* 13, 2914. HARRIET F. HOLMES

The excretion of "acetone" and nitrogen in nausea and vomiting of pregnancy. V. J. HARDING AND C. T. POTTER. *Brit. J. Exptl. Pathol.* 4, 105-16(1923).—The excretion of "acetone" in the majority of cases of nausea and vomiting of pregnancy parallels the clinical condition. The effect of abortion is to diminish the production of "acetone." Tissue destruction in nausea and vomiting of pregnancy when under the influence of small amts. of carbohydrates is governed by the demand for further supplies of carbohydrates. The results are similar to those observed in some cases of starvation but in pregnancy the demand for carbohydrate, and consequently the disturbance following its lack, is more intense than in starvation. HARRIET F. HOLMES

The precipitation of colloidal gold by cerebrospinal fluid; the diagnosis of neurosyphilis. JOHN MELLANBY AND THOMAS ANWYL-DAVIES. *Brit. J. Exptl. Pathol.* 4, 132-45(1923).—Colloidal Au neutral in reaction can be prepd. by adding 1 cc. of AuCl₃ (1%) to 100 cc. of boiling K₂C₂O₄ (0.01%). Pptn. of neutral colloidal Au is always produced by paretic cerebrospinal fluid, sometimes by tabetic fluid, but never by normal fluid. The pptg. substance is non-dialyzable, pptd. by 1/2 satn. with (NH₄)₂SO₄, pptd. by 5% alc. at 0°, destroyed by heat at temps. depending on the reaction of the fluid and the duration of heating. Neutral colloidal Au, sensitized by the addition of acid, may give a tabetic or paretic pptn. curve with normal cerebrospinal fluid, depending

on the degree of sensitization, and *vice versa* on desensitization by alkali. These facts emphasize the necessity of working with a neutral colloidal Au. Neutral salts have a small influence only on the sensitivity of colloidal Au to pptn. by cerebrospinal fluid. All cerebrospinal fluids contain not only a positively charged colloid which ppts. colloidal Au but also a negatively charged colloid which ppts. colloidal Fe and therefore antagonizes the pptg. action of the former on an Au sol. The positive colloid appears to be a "euglobulin," the negative colloid a "pseudoglobulin." In normal cerebrospinal fluids the "euglobulin" and "pseudoglobulin" are present in small quantities only, and the pptg. action of the "euglobulin" is balanced by the inhibitory action of the "pseudoglobulin," unless a Au sol. is used which has been sensitized by acid. In cerebrospinal fluid which gives the tabes pptn. curve the "euglobulin" is increased in amt. to a moderate extent, and to a larger extent in fluids which give the paretic pptn. curve. Possibly the pptn. curves stated to be characteristic of cerebrospinal syphilis, *i. e.*, absence of pptn. in low dilns. and complete pptn. in high dilns., are due to a large increase of both "pseudoglobulin" and "euglobulin" in the cerebrospinal fluid. H. F. H.

Some new principles in bacterial immunity, their experimental foundation and their applications to the treatment of refractory infections. GEORGES DRYER. *Brit. J. Exptl. Pathol.* 4, 146-76(1923).—The successes of bacterial therapy and prophylaxis are obtained in general with microorganisms of the non-acid-fast and Gram-negative varieties. Since acid-fastness and Gram-positiveness have been clearly proved to be associated with the presence in the bacterium of certain waxy, fatty or lipid substances, it seemed probable, *a priori*, that these substances were the cause of failure in immunization. By the successive application of formalin and fat solvents, the tubercle bacillus and other acid-fast bacteria were rendered non-acid fast and similarly Gram-positive microorganisms were reduced to a Gram-negative condition. The "defatted" bacteria were found to be capable of reacting with specific antisera, and this led on to the exptl. proof of their antigenic action in the animal body, where they gave rise on injection to the production of the well known immune substances such as bacteriolysins, complement-fixing bodies, precipitins and agglutinins. These antigens exerted definite curative effects on animals suffering from bacterial infections. The Gram-negative bacteria when made Gram-positive by the same treatment retained their ability to cause the production of immune substances, such as specific precipitins and complement-fixing substances. The "defatted" bacilli are readily digested by trypsin while untreated bacilli are in the main indigestible. Growth of the anthrax bacillus and of *Staphylococcus aureus* at 42-43° gives rise to a weakening or disappearance of Gram-positiveness, owing to a deficient formation of the normal "fatty" constituent. Such bacilli are easily disintegrated and the release of their antigens would cause a rapid immunity response. This may be the explanation of Pasteur's classical demonstration of the immunizing properties of anthrax bacilli "attenuated" by growth at 42-43°. The subcutaneous injection into animals of tubercle and staphylococcal "lipoids" obtained by extraction with acetone after treatment of the bacteria with formalin gave rise to a local infiltration, sometimes with ulceration. A larger dose of defatted bacilli caused no local reaction, indicating that the "lipoids" of the bacterial body form an important obstacle to the solvent and protective action of the body fluids, and cause the severe local reaction with infiltration and sometimes necrosis noted on subcutaneous injections of dead tubercle bacilli or staphylococci. H. F. HOLMES.

Experimental production of nuclear division by intraperitoneal serum injection. J. BERRERICH. *Centr. allgem. Path.* 33, 281-3(1923); cf. Dustin, *Compt. rend. soc. biol.* 85 No. 20(1921).—Injection of 2 cc. human serum into mice failed to stimulate the mitosis, and cell division in the thymus and other organs noted by Dustin. E. R. LOSG.

The immediate prognosis in nephritis, with some remarks on uremia. O. L. V. DE WESSELOW. *Lancet* 1923, II, 163-5.—The parallelism between blood urea and plasma P is of prognostic significance in nephritis. As the urea increases up to 400-500 mg. per 100 cc. plasma P may increase to 10-22 mg. per 100 cc. in fatal cases. E. R. L.

Further investigations on the trypanocidal substances of human serum. F. ROSENTHAL AND R. FREUND. *Z. Immunitäts.* 37, 48-76(1923).—The chief site of formation of the trypanocidal substances of human serum is the liver. The substances are found quant. in the eu- and pseudo-globulin fractions. They have no relation to fibrinoglobulin and albumin. They are not antigenic; no antibodies result from treatment of rabbits or mice. It is true that if animals are treated parenterally with active serum for some time, and then an interval is allowed to elapse, another injection of active serum fails to confer trypanocidal activity upon the animal injected. This phenomenon does not depend, however, upon the formation of antitrypanocidal substances but rather upon an exhaustion, by the first treatment, of a substance within

the body of the treated animal from which the animal would normally build trypanocidal substance. Human serum does not contain trypanocidal substances as such, but only trypanocidogenic, which on introduction into a suitable experimental animal are converted into true trypanocidal substance. It is doubtful if the trypanocidal activity of human serum plays an important role in the natural immunity of man to the etiological agents of animal trypanosomiasis.

E. R. LONG

New experiments on the diagnosis and therapy of diseases of hypersensitiveness (allergic diseases). W. STORM VAN LEEUWEN, Z. BIEN AND H. VAREKAMP. *Z. Immunitäts.* 37, 77-105(1923).

E. R. LONG

Investigations on the nature of bacteriolytic substance. K. HAJÓS. *Z. Immunitäts.* 37, 147-51(1923).—The lytic action of exts. of feces and duodenal juice upon dysentery bacilli was studied. The exts. which were actively lytic lost none of their lytic property upon filtration through a Berkefeld filter. The size of the particle of the lytic substance is not greater than the albumin mol. Actively lytic exts. could be made more active, and inactive ones made actively lytic by filtration through a Haen membrane; inhibiting substances or antilyns are apparently held back. It is recommended that for the demonstration of lysis exts. be filtered through a Haen membrane instead of a Berkefeld filter.

E. R. LONG

Immunity and natural resistance. LUDWIG GÓZONY AND EUGENE KRAMAR. *Z. Immunitäts.* 37, 152-64(1923); cf. *C. A.* 17, 2297.—Parasitism and saprophytism in a given host are correlated with the ability of a given organism to reduce methylene blue and other substances while in contact with the serum of that host's serum. The serum of susceptible animals furthered reduction; that of insusceptible animals did not. For example, human serum greatly increased the reducing activity of gonococci; the serum of the insusceptible ox was much less effective. A general rule for several bacteria and several animals of varying susceptibility to infection with these bacteria could be drawn. To rule out the non-sp. influence of serum protein in the demonstration of the reduction-furthering activity it is best to dilute serum 1:400.

E. R. LONG

Serum hemolysin and cholesterol. W. WEIS-OSTBORN. *Z. Immunitäts.* 37, 165-9(1923).—The inhibiting action of cholesterol upon autohemolysins in paroxysmal hemoglobinuria, observed by others, is noted and previous observation confirmed. Colloidal starch, albumin and globulin solns. may weaken this inhibiting action. This fact may explain the occasional failure of cholesterol therapy in paroxysmal hemoglobinuria.

E. R. LONG

An antagonism between albumin and globulin and its use in serum diagnosis. G. A. BROSSA. *Z. Immunitäts.* 37, 211-20(1923).—Serum globulin favors the pptn. of colloidal Congo red by electrolytes. Serum albumin protects against pptn. In mixts of the two there is a combination of action. The effect, sensitizing or protective, will depend upon which protein is present in excess. On this basis the globulin-albumin ratio of mixts. of unknown compn. can be estd. By this method previous results for various animal species have been confirmed. It has also been useful in the study of pathol. serums. Typhoid and other serums giving flocculation and agglutination reactions also show a change in the globulin-albumin ratio, detectable by their effect upon Congo red. Cf. *C. A.* 17, 1487.

E. R. LONG

Prolonged hypodermoclysis with antigens. ALFONS GERSBACH. *Z. Immunitäts.* 37, 228-37(1923).—Prolonged subcutaneous injections of bacteria into rabbits were as ineffective as single large injections in producing those types of infection to which the rabbit is naturally resistant. However, extraordinary increase in agglutination titer was effected by this method, which should have practical application in the production of immunity.

E. R. LONG

Differentiation of various proteins by the Abderhalden reaction, particularly urine proteins. FUSAO ISHIWARA. *Z. Immunitäts.* 37, 238-48(1923).—The Abderhalden reaction is modified. For the prepn. of antigen, heat the protein-contg. fluid with NaCl and HOAc, and wash the coagulated protein 2-3 times in boiling water, or until it gives no reaction with ninhydrin. Place 0.05 g. of this in a dialyzing tube, add 1.2-1.5 of the serum to be studied, cover with toluene and place in the incubator 13-14 hrs. To 5 cc. dialyzate add 2 drops 1% ninhydrin and place the tubes in a current of steam 15 minutes or until the violet color appears, but not more than 25 min. Urine protein of chronic, acute and pregnancy nephritis can be identified; plant and animal proteins can be distinguished; different organs of the same animal can be distinguished; cooked and spoiled horse flesh can be distinguished from other animal meats.

E. R. LONG

Recognition of the heterogenetic antigen-antibody reaction. F. GEORGI. *Z. Immunitäts.* 37, 285-314(1923).—Biological testing of the flocculi of such heterogenetic

antigen-antibody reactions as sheep anti-rabbit corpuscle serum against guinea pig kidney ext. shows that their anticomplementary action is destroyed at 100°. The native ppt. is weakened in its anticomplementary action by addition of antiserum, and increased by addition of ext. The heated ppt. takes on anticomplementary activity on addition of antiserum, while ext. is without action. As a result of the heating of the flocculi, components must be put out which apparently correspond in their function with heterogenetic antigen. One might assume that in the heterogenetic reaction, as well as in positive serological recognition of lues, the flocculi consist of a nucleus predominantly lipoidal, surrounded by thermolabile serum components. The anticomplementary action occurs also if the ext. is treated with EtOH; it persists at 0°, and is not noticeably increased by digestion of the mixt. before the addn. of blood. Under certain conditions by the action of antiserum alone on complement an anticomplementary action can develop. It is less than on the addition of EtOH, and still less than on ext. addition. Heterogenetic antisera seem more strongly anticomplementary than other antisera. There is a quant. increase from rabbit sera up, so that it is questionable if the heterogenetic antisera possess any sp. function in this respect. There may be a combined action with the antigen present in guinea pig serum. Probably in the course of immunization an increased lability of serum proteins in the sense of a globulin increase occurs, so that the tendency of sera to be anticomplementary is increased. Ale. organ exts. of heterogenetic type do not cause antibody production. Simultaneous injection of ale. guinea pig kidney ext. and aq. rabbit kidney ext. produces no immunization. No increase in immunity occurs as a result of treatment with ale. organ exts. following first treatment with aq. guinea pig kidney ext. Simultaneous use of ale. guinea pig kidney ext. and horse serum leads to no recognizable amboceptor formation, although it is to be assumed that in horse serum heterogenetic antigen is present in small amt.

E. R. LONG

Contribution to the serology of the cerebrospinal fluid. V. KAFKA. *Z. Immunitäts.* 37, 315-26(1923).—A study of the complement function of cerebrospinal fluid. Every spinal fluid hemolyzes sensitized sheep corpuscles upon addition of the end piece of complement, prepd. from a variety of sera by acid treatment. The phenomenon is thermolabile. The substance responsible can be removed by shaking the fluid with ether. It is the middle piece of complement. Active and inactivated fluid agglutinate highly sensitized corpuscles, the strength of agglutination paralleling the degree of sensitization. The Wassermann reaction in the spinal fluid can occur in the complete absence of globulins; it is not conditioned by their presence nor by their increase nor physical state.

E. R. LONG

The amylase content of the pericardial fluid. N. MATSUMOTO. *Intern. Med. News (Japan)* 42, No. 4 (1923); *Japan Med. World* 3, 164.—Amylase was demonstrated in the pericardial fluid in 3 cases of pericarditis. The amylase content of the thoracic cavity fluid was greater. Neither the severity of the disease nor the lapse of time after death influenced the amylase content.

M. E. MAVER

The carbohydrate metabolism of transplanted tumors. I. K. TADENUMA, S. HOTTA AND J. HOMMA. *Japan Med. World* 3, 71-4(1923).—The blood sugar in the normal wing varied from 0.16 to 0.236%. In the wing with the tumor it varied from 0.14 to 0.21%. In 9 cases out of 10 the blood sugar value was lower in the wing with the tumor, the decrease being from 0.1 to 0.4%. When hyperglucemia was produced by the injection of glucose, the blood of the normal wing contained from 0.147 to 0.442%, while that in the wing with the tumor contained from 0.002 to 0.0716% less. When the hyperglucemia was produced by the injection of adrenaline, a smaller quantity of sugar was always found in the wing with the tumor, the difference in one case being 0.06%. The tumor was stimulated by massage, causing a similar increase in the consumption of sugar by the tumor.

M. E. MAVER

Serum albumin in beriberi. A. SHIGEMARU, Y. OKAMOTO AND S. TAKIMOTO. *Med. News (Japan)* No. 1011 (1923); *Japan Med. World* 3, 165.—In edematous beriberi the serum albumin varies from 6.5 to 6.9%, the normal being 6.9-9.0%. After recovery from the edema a concn. higher than normal is often found, which may be due to the condensation of the blood after diuresis. A variation in the albumin content is seen after a normal state of water metabolism is attained.

M. E. MAVER

Etiology of pellagra. L. RANDOIN. *Bull. soc. hyg. aliment.* 11, 364-77(1923).—A review with bibliography.

A. PAPINBAU-COUTURE

The reaction of antigen and antibodies after adsorption of one of these by charcoal. M. v. EISLER. *Biochem. Z.* 135, 416-41(1923).—Various amts. of toxin or antitoxin plus 0.1 g. C are made up to 2 cc. with 0.85% NaCl. The mixts. are centrifuged after standing 0.5 hr. The supernatant fluid and a suspension of the pptd. C in 0.85%

NaCl are tested separately for adsorption and for the action of adsorbed toxin on its antitoxin or *vice versa*. Each of the adsorbed antitoxins loses its ability to combine with its toxin. C treated with antitoxin and then with toxin is more toxic than C treated with toxin alone. This is because the adsorbing surface is already occupied by antitoxin and the toxin is therefore not adsorbed. The adsorbed toxins, on the other hand, do not all act alike. C which has adsorbed vibrio hematoxin retains its ability to combine with the antitoxin; C which has adsorbed diphtheria or tetanus toxin loses this ability to combine with the antitoxin. From the results of these and similar expts., certain analogies are suggested.

GEORGE ERIC SIMPSON

The colloid stability of serum toward the oligodynamic action of metals and its diagnostic value. RUD. REITLER. *Biochem. Z.* 136, 449-68(1923).—In 14 test-tubes are prepd. 2 cc. of serum dild. with 0.9% NaCl in the proportion 1: 2; 1: 4; . . . 1: 16,000. In each is suspended a thin copper plate 1 cm.² These are kept at 37° for 1 hr. and in refrigerator 20 min. In normal sera, max. amt. of pptn. is found in the 1: 64 dild., and the greatest dildn. showing flocculation is 1: 250. Various pathol. sera were tested. In tuberculosis the reaction may be of diagnostic value. In tuberculosis and malaria the limit of flocculation is higher (1: 500), and the point of max. flocculation lower (1: 32), than normal. Cachexia in either case interferes with characteristic results. Preliminary studies on the mechanism of the reaction are reported. "The reaction is not simply an expression of the stability of the colloids."

G. E. SIMPSON

The mechanism of the miostagmin reaction. L. F. LOEB. *Biochem. Z.* 136, 190-7(1923).—The surface tension of serum is decreased on addn. of an alcoholic linoleic-ricinoleic acid soln. (0.5 cc. linoleic acid + 0.2 cc. ricinoleic acid + 10 cc. abs. alc.). The micellae subsequently adsorb some of the acid, so that its concn. is decreased. As a result the surface tension increases, but does not attain its original value. The secondary increase is less with pathol. than with normal sera. The reason for this is not clear. Perhaps a change in degree of dispersion or in concn. of the micellae occurs. For a description of the mode of experimentation, cf. *C. A.* 4, 938.

G. E. S.

The ability of blood serum to hydrolyze glycogen. DIONYS FUCHS AND GÉZA HÉTÉNYI. *Biochem. Z.* 136, 469-70(1923).—Sera of diabetics and non-diabetics were mixed with 1% glycogen. The rotation was greater in the soln. contg. diabetic sera, which therefore possess greater ability to hydrolyze glycogen than other sera. Eighty cases were examd.

GEORGE ERIC SIMPSON

Chemistry of pseudochylous ascites and other types of exudates. R. B. GIBSON AND C. P. HOWARD. *Am. J. Med. Sci.* 166, 80-9(1923).—A milky peritoneal fluid from a case of malignancy was characterized by a high content of lecithinophosphoric acid with some increase in the amt. of cholesterol. The fatty acids were low. The opacity of the fluid was not due to Ca in combination with protein.

G. H. S.

The alkali reserve of the cerebrospinal fluid in various states of the central nervous system. RAPHAEL ISAACS. *Am. J. Med. Sci.* 166, 237-43(1923).—No direct relationship could be established between the CO₂-combining power of the spinal fluid and the type of disease. A difference in CO₂-combining power was observed in fluids at different levels around the brain and cord, the variations being from 0 to 24 vol. %. In the absence of nervous symptoms the av. combining power of the spinal fluid (lowest fraction) was 50.7 vol. %. In patients with headache the corresponding value was 38.9; in unconscious patients, 39.5; in delirium and mania, 41.66; in those who were stuporous, semicomatose, hazy, or drowsy, 41.58; in convulsions, 43.37. The values found appeared to correspond more closely to the symptom-complex than to the basic disease process. Negative Wassermann reaction fluids gave a value (av.) of 49.1 vol. %; positive Wassermann fluids, 44.3. Fluids with negative globulin averaged 45.87; those with positive globulin, 41.14. Fluids under normal pressure were 49.36, with increased pressure, 42. With normal cell counts, 48.5, with cells 8 and above, 43.1. There was no parallelism between the reaction of the fluid (which varied at different levels) and the alkali reserve. Changes in the alkali reserve could not be correlated with the progress of the disease. In pathological states the CO₂-combining power of the fluids varied within wider limits than in normal conditions.

G. H. S.

Creatininemia; based upon a study of 1500 blood chemical analyses. H. M. FEINBLATT. *Am. J. Med. Sci.* 166, 249-56(1923).—A study of the blood analyses made upon 1500 unselected cases showed values for blood creatinine above 2.5 mg. per 100 cc. in 43 cases. In all of these there was evidence of disturbed kidney function. With the higher values, from 5 to higher than 10 mg. per 100 cc., the mortality was practically 100%.

G. H. S.

Changes in resistance to hemolysis of erythrocytes brought about by feeding cholesterol and fats. D. RYWCOSCH. *Arch. ges. Physiol.* (Pflüger's) 196, {643-5

(1922).—White rats were fed (in continuation of earlier expts. upon sheep) with cholesterol and beef fat for a long time. When their erythrocytes were tested for susceptibility to hemolysis it was found that they had become abnormally sensitive to lysis by water but that they had developed an increased resistance to saponin hemolysis.

G. H. S.

Production of heterogenetic antibodies with mixtures of the binding part of the antigen and protein. K. LANDSTEINER AND S. SIMMS. *J. Exptl. Med.* **38**, 127-38 (1923).—The EtOH-sol. ext. of heterogenetic antigen, which possesses the sp. chem. structure of the entire antigen, has a detectable but generally very slight power to increase the amt. of heterogenetic antibodies, when injected into rabbits. This substance can be transformed into an efficient antigen by mixing it with protein solns. such as diluted normal serum. Such mixts. are considerably more active than the same substances injected separately. Therefore, the effect of the serum is probably due to the formation *in vitro* of a loose compd. between the EtOH-sol. substance and protein, the compd. acting as a complete antigen. It may be supposed that there exists a group of natural antigens which are built up of 1 sp. reacting part that is almost or entirely devoid of antigenic properties and another part, a protein, responsible for the immunizing effect.

C. J. WEST

Studies on pneumococcus immunity. III. The nature of pneumococcus antigen. WM. A. PERLZWEIG AND G. I. STEFFEN. *J. Exptl. Med.* **38**, 163-82 (1923).—Mice may be actively immunized with the protein fraction obtained by treating pneumococci with anhydrous Na_2SO_4 or by soln. of pneumococci in bile salts and pptn. with EtOH. Pneumococcus antigen is carried within or adheres to the protein fraction of the organism. The antigen is resistant to prolonged autolysis and to tryptic digestion and can be recovered from the sol. portions of digests of either the intact bacteria or the bacterial protein. It may be isolated from each of the 3 fixed types of pneumococcus by tryptic digestion of the pneumococci and extn. of the digest with 70-90% EtOH. The antigen is not sol. in abs. alc., nor in Et_2O or other lipoid solvents. The immunizing property of slightly acid solns. of the antigen is not impaired by boiling for 5 min., nor by heating at 56° for 1 hr. Sterile unpreserved solns. of the antigen did not deteriorate by standing in the refrigerator for 3.5 months. The exact chem. nature of the antigen is as yet unknown. It appears that it is non-lipoidal, and that it probably adheres to the protein fraction in a loose chem. or physical union rather than representing a protein complex of large mol. size. Some of the antigens studied have been shown to contain a non-sp. factor promoting the growth of bacteria. The purified pneumococcus antigen solns. are non-toxic for mice.

C. J. WEST

H—PHARMACOLOGY

ALFRED N. RICHARDS

Study of the mechanism of the action of the nervi vagi and of cardiac remedies.

HENRIJEAN. *Bull. acad. roy. med. Belg.* [5], **3**, 371-90 (1923); cf. *C. A.* **17**, 2451. H. studies the effect of injections of 0.1-0.2 mg. ouabaine (solubaine "Nativelle") and of KCl and CaCl_2 in a dog after section of one vagus.

R. BRUTNER

The proof of binding of pilocarpine and rabbit serum by means of a chemical method. L. JENDRASSIK. *Nederland. Tijdschr. Geneeskunde* **67**, **11**, 404-5 (1923).—When rabbit serum is mixed with pilocarpine and let stand for $\frac{1}{2}$ hr., pilocarpine cannot be pptd. by iodine; this proves that it has been bound. Immediately after mixing pptn. does take place. Also in *Arch. exptl. Path. Pharmacol.* **98**, 118-22 (1923).

R. BRUTNER

Further communications on the binding of alkaloids to constituents of the serum. R. BRUTNER. *Nederland. Tijdschr. Geneeskunde* **67**, **11**, 405-6 (1923); cf. preceding abstract.—While alkaloids diffuse rapidly, serum proteins are kept back by parchment membranes; therefore, the alkaloid which is bound to a protein will also be kept back. Expts. proved this to be the case; e. g., if equal vols. of rabbit serum and $\frac{1}{2}\%$ pilocarpine soln. are mixed, and—after $\frac{1}{2}$ hr.—are placed in a parchment hull, and dialyzed against pure water, no alkaloid can be detected in the outside liquid. The same expt. can be produced with the serum of cattle or of horse but a smaller amt. of pilocarpine is bound in this case. Also other alkaloids may be used, e. g., atropine, strychnine, novocaine, or cocaine.

R. BRUTNER

Experimental researches on the "nitritoid crisis" from arsenobenzenes. I. Present status of the question. Anaphylactic tests. ATTILIO BUSACCA. *Arch. farm. sper.* **36**, 37-48 (1923).—In the guinea pig, a 2nd injection of nearsphenamine, after an interval of a few days up to 14 days according to the method employed, results in the so-called

crisis. A 3rd and even a 4th injection at intervals of a few days do not prevent the occurrence of this crisis. Three degrees of nitritoid crisis are noted, a mild, a severe and a fatal form, the last being preceded by the other 2, but resulting in convulsions and death after 12-24 hrs. These 3 forms are independent of the dose and are determined more by individual susceptibility. In the fatal cases autopsy revealed only a congestion of all the organs. The mechanism of the reaction is the same as that of anaphylaxis.

A. W. DOX

The central influence of atropine and hyoscine on the heart rate. W. J. R. HEINEKAMP. *J. Lab. Clin. Med.* 8, 104-11(1922).—Small doses of atropine (0.0003 g. in dogs and 0.001 g. in man) produce inhibition of the heart owing to direct stimulation of the cardio-inhibitory center. Hyoscine exerts a similar action to that of atropine on the medulla of *Pseudomys troostii*, except that the primary stimulation is followed by depression.

E. R. LONG

The action of morphine, codeine and apomorphine as shown by perfusion of the medulla of the terrapin (*Pseudomys troostii*). W. J. R. HEINEKAMP. *J. Lab. Clin. Med.* 8, 165-9(1923).—Morphine sulfate when perfused through the medulla of the terrapin produces inhibition of the heart, owing to its products of oxidation, since morphine oxidized *in vitro* with HNO_3 when perfused exerts a quicker and more powerful stimulating action than morphine itself. Codeine exerts no influence on the medulla, probably because of the presence of a methoxy group. However, when oxidized it too has a powerful stimulating effect. Apomorphine first stimulates and then paralyzes the medulla. Solns. which have been exposed to air and hence oxidized are ineffective.

E. R. LONG

Chemical changes of the blood under the influence of drugs. II. Morphine. H. V. ATKINSON AND H. N. ETS. *J. Lab. Clin. Med.* 8, 170-5(1922).—Morphine increases the CO_2 -combining power of the plasma, and the following constituents: sugar, creatinine and total fat. Lecithin, cholesterol and O_2 -combining power are decreased.

E. R. LONG

Observations on the action of germanium dioxide in pernicious anemia. M. E. ALEXANDER. *Am. J. Med. Sci.* 166, 256-61(1923).—Germanium dioxide appeared to be less effective in modifying the hemoglobin content and the erythrocyte count than are As and Fe.

G. H. S.

The action of neutral salts upon the tonic portion of muscular contraction. S. M. NEUSCHLOSZ. *Arch. ges. Physiol.* (Pflüger's) 196, 503-30(1922).—Very slight increases in the amt. of K in Ringer soln. augment the internal tonus of isolated frog muscle during rhythmic stimulation. Increase in the Ca content, or removal of the K, has an opposite effect. In addition, high concns. of Ca inhibit the development of rigor. The veratrine effect is favored by small amts. of CaCl_2 and inhibited by KCl . With large amts. of CaCl_2 the veratrine effect is abolished, but the mode of action with Ca differs from that obtained with K. BaCl_2 favors the veratrine effect. In general, Ba in high concns. acts like Ca in low concns., the reason for the quant. differences being associated with the slight permeability of the surface layers of the muscle for Ba ions. Ions, such as oxalate and citrate, which ppt. Ca and at the same time react on colloids, cause a double effect upon isolated muscle after the manner of veratrine. The effects of ions upon the tonus of muscle are due to a two-fold action, involving, first, the colloidal state of the sarcoplasm, and, second, the permeability of the surface layers of the fibers.

G. H. S.

Pharmacology of body position and labyrinthian reflexes. VII. Oil of chenopodium. J. J. JONKHOFF. *Arch. ges. Physiol.* (Pflüger's) 196, 571-83(1922).—Oleum chenopodii was administered to rabbits by either intravenous or subcutaneous injection. In either case the intoxication phenomena were associated with a complete loss in all of the otolith reflexes, while those of the semi-circular canals remained unchanged or were strengthened.

G. H. S.

I—ZOOLOGY

R. A. CORTNER

The duration of the stay of the ingested leaf in the intestine of the silk worm. P. LORENZA LOMBARDI. *Ann. scuola agr. Portici* [2] 15, 1-10(1920).—Dyed leaves were fed. The colored leaves appeared in the droppings $1\frac{1}{2}$ - $2\frac{1}{4}$ hrs. after ingestion; the greater portion of the colored leaves disappeared from the droppings $2\frac{1}{2}$ - $5\frac{1}{4}$ hrs. after ingestion of normal leaves; and total disappearance required 6-10 hrs. dependent upon the maturity of the larvae.

ALBERT R. MRRZ

Influence of increasing p_{H} of the sea water on the rapidity of the segmentation of eggs of *Halosydna* and of *Sabellaria*. ALPHONSE LABBÉ. *Compt. rend.* 176, 1423-6

(1923); cf. *C. A.* 16, 2938.—Increasing the p_{H_2} of sea water from 8.1 to 8.4 by the addn. of NaOH decreased the time required for segmentation nearly one-half. L. W. RIGGS

Food and parthenogenetic reproduction as related to the constitutional vigor of *Hydatina senta*. W. V. LAMBERT, W. S. RICE AND H. C. A. WALKER. *Biol. Bull. Marine Biol. Lab.* 44, 192-202(1923).—This exptl study with *Hydatina senta* was made to det. if possible whether the gradual loss of vigor is due to the parthenogenetic reproduction, or to a too restricted diet. Complete details are given. The opinion appears justified that the constitutional vigor of Race A, fed upon an exclusive colorless diet (*Polytoma*), was noticeably weakened, while that of Race B, fed upon a diet of *Polytoma* plus a green food contg. carbohydrates, was sustained and even raised above that of the wild races. Decline in vigor appears to follow an unbalanced diet rather than the parthenogenetic method of reproduction. L. W. RIGGS

12—FOODS

W. D. BIGELOW AND A. E. STEVENSON

The distribution of vitamins in nature. W. D. RICHARDSON. *Bull. Inst. Marine Mfrs.* No. 5, 42 pp.(1923).—Review of history of the discovery of vitamins, their function and distribution with tables showing quant. occurrence in natural foodstuffs.

H. B. LEWIS

A comparison of roughages for milk production. A. C. McCANDLISH AND EARL WEAVER. *Iowa Agr. Expt. Sta., Bull.* 212, 275-86(1923).—Corn silage and alfalfa hay are the best roughages for dairy cattle. Corn fodder and timothy are very poor. The dry matter in silage is worth about twice that in fodder; and that in alfalfa about 17 times that of timothy hay as shown by the production of milk and butter fat. In combination with other feeds timothy has greater value than when alone, but should not be used on a dairy farm.

M. S. ANDERSON

Investigation of different methods of testing Babcock milk bottles. C. O. WILLIAMS (B. J. SMIT given as author by mistake in the original). *S. African J. Sci.* 19, 132-6(1922).—Of the 3 methods described, (1) a volumetric method, (2) a gravimetric method using distd. water and (3) a gravimetric method using Hg, the first named is regarded as the best one for ordinary use.

E. J. C.

Pipet for lactose determination in milk. E. G. MAHIN. *Ind. Eng. Chem.* 15, 943(1923); 1 cut.—The special feature of the app. is the graduation on the stem from 63.5 up to 64.85 cc. in divisions of 0.05 cc., so that the entire vol. of milk of a predetermined sp. gr., read from a table in the Official Methods, may be measured at one time.

J. H. MOORE

Sodium hypochlorite. III. Rate of decomposition in cow milk. H. F. ZOLLER. *J. Dairy Sci.* 6, 319-19(1923).—Relative rate of chlorination by NaOCl of raw whole, boiled whole and skimmed milk was detd. by means of an adopted α -1-starch paste method. There was no noticeable difference in the rate of chlorination, although boiled milk showed negative methylene blue and negative Schardlinger reactions. Selective action of sp. substances in milk is negated by this examn. The absorption of Cl from NaOCl is very rapid at first, and then slows down as the milk becomes satd. The temp. affects the rate of chlorination; raising the temp. from 20° to 60° decreases the time of chlorination to $\frac{1}{10}$ of that required at 20°. Small changes in p_{H_2} failed to exert much influence upon the rate of reaction. Pure sodium caseinate freshly prepd. is chlorinated very rapidly, and is believed to be the chief Cl-absorbing substance in milk. H. F. Z.

The precipitation of milk proteins by copper salts. A. J. J. VANDELDE. *Lait* 3, 437-47(1923).—A review of the literature covering Cu-protein combinations is made in order to det. whether any stoichiometric relationship exists. Mitscherlich and Gullotti in sep. investigations concluded that the Cu salts are bound *in toto* in the Cu-protein ppt. V. studied the problem from the standpoint of the combination of sep. ions, $CuSO_4$, $CuCl_2$, $Cu(NO_3)_2$ and $Cu(CH_3COO)_2$ being used. The results show that only the cation, Cu, was bound by the milk proteins, and this in varying quantities, depending upon the concn. of Cu soln. employed. The ppts. held from 5 to 1.5% of Cu.

H. F. ZOLLER

Whipped cream. LUHRIG. *Pharm. Zentralhalle* 64, 319-22(1923).—Descriptive of expts. involving the detn. of phys. constants of goat milk fat and cow milk fat isolated from whipped cream taken in a seizure case.

W. O. E.

Copper in dairy products and its solution in milk under various conditions. F. R. RICE AND J. MISCALL. *J. Dairy Sci.* 6, 261-77(1923).—Earlier work on the effect

of the presence of Cu in dairy products is reviewed. Strips of pure Cu were allowed to stand in contact with milk in glass vessels under different conditions. Cu was detd. on the ash obtained from this milk in most cases electrolytically, though where the amt. was small it was detd. colorimetrically by the K ethylxanthate method. The presence of air or O₂ increased enormously the amt. of Cu dissolved by the milk. Cu with an oxide incrustation such as results from exposure to air or the oxidizing portion of the gas flame, or when bathed with solns. of NaOCl, yielded much more readily to soln. than a smooth bright surface of the metal. CO₂ did not increase the solvent action of the milk and the presence of sucrose affected it but little. Milk warmed to 62.8° dissolved much more Cu than at boiling, while the amt. dissolved at room temperature was about the same as at boiling. The fact that milk once boiled dissolved no more copper at 62.8° than at boiling indicated that the higher heat destroyed some condition which contributed to the solvent power. Slight increases in acidity increased very slightly the amt. of Cu dissolved. Upon separating a quantity of milk which contained Cu it was found that the metal distributed itself between the skim milk and cream in proportion to the wt. of the two fractions; it was evident that the Cu was not dissolved in the fat. As was postulated from electrochemical relations, it was found that in presence of Sn less Cu was dissolved in milk than from a Cu surface alone.

FRANK E. RICE

Some determinations on the soluble nitrogen compounds of cream and butter. L. W. FERRIS. *J. Dairy Sci.* 6, 320-9(1923).—The purpose was to find how butters made from samples of cream varying in age and quality differed with respect to keeping quality and to some of the sol. nitrogenous constituents. Ammonia N was detd. by adding 4 g. Na₂CO₃ dissolved in a little water and aerating the mixt. into standard acid. After aeration the fat was removed by shaking with gasoline and the residue made up to 500 cc. For detg. "nitrogen not pptd. by phosphotungstic acid" 25-cc. aliquots were taken to which was added 10 cc. of 5% H₂SO₄ and 10 cc. of a soln. of 5% phosphotungstic acid in 5% H₂SO₄ and the mixt. set aside 14 hrs. On filtering, the ppt. was washed with 2.5% phosphotungstic acid in 2.5% H₂SO₄ until filtrate and washings reached 100 cc. N detn. was made by means of the Kjeldahl method. Amino N was detd. on a soln. prepd. by taking a 50-cc. aliquot, warming to 40° and adding a soln. of 5% Na₂SO₄ in 5% CH₃COOH until slightly acid to Me red and allowing to stand 16 hrs. Upon filtering, the ppt. was washed with water until filtrate and washings amounted to 200 cc. This was evapd. to 15 cc., filtered, and the ppt. washed with small amts. of water until the filtrate measured 20 cc. Amino N was detd. on 5-cc. aliquots of this soln. in the Van Slyke app. In making the detns. on butter, 600 g. was weighed into a quart jar, melted at 50°, the fat partly siphoned off, and the remainder removed with gasoline. Detns. on the residue were made by a procedure similar to that followed with the cream. On some of the samples detns. were made of "amino nitrogen in acetic acid and picric acid filtrate" by a method similar to that previously described (*C. A.* 17, 156). Sol. N compds. were generally higher in samples of butter of lower quality and in butter held in cold storage. Greater proteolysis was indicated in butter made from sweet cream than from pasteurized cream, also greater for sour cream than sweet cream. Since inoculating cream with various organisms did not in most cases affect the amt. of sol. N compds. in the butter, it was concluded that "cream already contained enzymes or organisms sufficient to produce considerable proteolysis."

FRANK E. RICE

The production of volatile fatty acids and carbon dioxide by propionic acid bacteria with special reference to their action in cheese. R. H. SHAW AND J. M. SHERMAN. *J. Dairy Sci.* 6, 303-9(1923).—It was purposed to gather information as to what substances in cheese could act as sources from which bacteria produce compds. which give the characteristic properties to the Emmenthal type of cheese. *Bact. acidi-propionici* (*d*) was inoculated into media contg. 1% of peptone, together with various test substances; after the incubation period there were detd. CO₂, total volatile acids, propionic and acetic acids. All these were found to be produced through the action of the organism on succinates, glycerol and peptone, also on lactose and lactates which had been previously known. Aspartic acid served as a source of acetic acid and CO₂ only. The action of the organism on butter fat was suspected but not definitely established. Formic, acetic, propionic, butyric and isobutyric acids were not attacked.

FRANK E. RICE

Determination of ash, arsenic, copper and zinc in gelatin. R. M. MERRIN. *Ind. Eng. Chem.* 15, 942-3(1923).—At the Meat Inspections Lab., Washington, during last year 247 samples of gelatin were examd. for As, Cu and Zn, and these were usually present in amts. not exceeding 1.4, 30 and 100 parts per million, resp. All the available methods for the detn. of As, Cu and Zn in food were tried out and found unsatisfactory when applied to the detn. of these metals in large numbers of samples of gelatin. The method described is free from all the faults cited against the older methods, and is given

in such complete detail as to be successfully handled by the inexperienced analyst.

Purification plant for oysters from polluted water. L. W. RIGGS. *Eng. News-Record* 90, 1047 (1923).—A plant at Inwood (L. I.), N. Y. is successfully disinfecting oysters from polluted waters. Two concrete basins each 22 x 25 ft. in plan by 1.5 ft. deep, with a capacity of 6000 gal. each, are capable of handling 400 bushels of oysters in 24 hrs. Disinfection is accomplished by electrolysis with the production of NaClO.

FRANK BACHMANN

A study of the factors affecting the jelling of fruits. L. W. TARR. Delaware Agr. Expt. Sta., *Bull.* 133, 14-15 (1923).—It is necessary to have pectin, sugar and acid present in the production of fruit jellies. It was established that 62.5 g. of sugar to 1 g. pectin was the optimum sugar-pectin ratio. The formation of jelly depends not upon the total quantity of acid present but upon the concn. of H ions. H₂SO₄ required 0.0295 g. per 1 g. of pectin to produce a jelly; acetic acid required 1.75 g. The H-ion concn. of the juices in each case was approx. p_H 3.4. A jelly could not be produced with a concn. less than this. The optimum concn. was p_H 3.1.

J. J. SKINNER

Formation of maltose in sweet potatoes on cooking. H. C. GORR. *Ind. Eng. Chem.* 15, 938-40 (1923).—The presence of maltose in cooked sweet potatoes is shown by the agreement of the quantity of sugars detd. by Cu reduction with the quantities measured by polarization, and by its isolation in the cryst. form. Sugar is not formed at the b. p. It is formed very rapidly during the initial stages of digestion of the sweet potato in water at a temp. range in which diastase is active, and appears to be due to the action of diastase on starch. The diastatic power of sweet potatoes has a practical bearing in cooking, canning, and making sirup or distd. products. The effect of cooking on whole, sliced, and finely divided sweet potatoes was detd. and a method for the prepn. of cryst. maltose was described.

L. W. RIGGS

Chemistry in the cereal industries. C. H. BAILEY. *Ind. Eng. Chem.* 15, 900-1 (1923).

E. J. C.

Why does lemon make the color of tea lighter? MARCEL DUVAL. *Bull. soc. hyg. aliment.* 11, 378-9 (1923).—The action is due entirely to the acidity of the lemon. Tea behaves similarly if an equiv. amt. of HCl is added. The original color is restored by neutralizing with NaOH.

A. PAPIERAU-COUTURE

The domestic production of protein. GERLACH AND FINGERLING. *Mitt. deut. Landw.-Ges.* 38, 352-5, 362-6 (1923).—The production of raw protein for stock food in Germany is at present only 60% of the actual requirement. It is proposed to meet this deficiency by increasing the production of food plants rich in protein; by N fertilization of grain-bearing legumes, clovers, meadows, and pastures; by more efficient conservation of green feeds rich in protein; and by feeding N to stock in the form of urea. The proposed remedies are discussed at length.

K. D. JACOB

Chemical studies of *Dolichos bulbosus*. L. THON. *Bull. agr. Congo Belge* 14, 51-4 (1923).—Chem. studies were made of nodules from the legume, *Dolichos bulbosus*, in different stages of development and of the ripened seeds. The tubercles contained 87.8% H₂O when young, 88.3% when plants were flowering and 84.7% when seeds were ripe. On a H₂O-free basis analyses of tubercles showed the following limits: ash 4.17-5.31%, fats 0.37-0.50%, total N 1.56-2.10%, non-nitrogenous material 70.83-80.95%, cellulose 4.37-4.97%. Feeding expts. showed that the coeff. of digestibility ranges from 53 to 70. Seeds showed the following compn. on dry basis: ash 4.76%, fats 20.50%, total N 4.77%, non-nitrogenous material 37.04%, cellulose 7.89%.

M. S. ANDERSON

Determination of hydrogen-ion concentration of milk (RICE, RIDER) 11B. Chemical studies of pombi (PIERALRTS) 27. Application of cryoscopy in pharmacy and food chemistry (DANKWORTT) 17.

Raw yeast. H. PLAUSSON. *Can.* 233,179, July 31, 1923. The digestibility of raw yeast is improved by heating it with H under high pressure.

Pretreating dried yeast to increase its baking strength. A. W. HIXSON. U. S. 1,464,710, Aug. 14. Dried yeast which it is desired to improve with respect to its baking strength, or even ordinary compressed yeast which is to be similarly improved, is allowed to stand for some time (e. g., 12-24 hrs.) in a fermentable sugar soln. of about 4° to 6° Balling. A suitable soln. may be formed from malt ext. with the addition of small amts. of vinegar, CaSO₄, Ca phosphate, K H tartrate, NH₄H₂PO₄ and NaCl.

Apparatus for pasteurizing milk or other liquids. M. GOLDBERGER. U. S. 1,464,704, Aug. 14.

Separation of xanthine derivatives from coffee beans, etc. N. ROSEWATER. Brit. 192,745, Oct. 13, 1921. Coffee beans and other natural cellular structures contg. xanthine derivs. are purified by heating to a temp. at or above the vaporizing point of the xanthine derivs. without carbonization or alteration of the remaining constituents. According to an example coffee beans are placed in a gas-tight receptacle and subjected to the action of steam or hot air or gas under pressure at a temp. of 250-455° F. The caffeine is carried off by the gas and may be treated with or without previous roasting or comminuting. Cf. *C. A.* 16, 992.

Flavoring beverages. I. A. VON HORST. U. S. 1,464,520, Aug. 14. A flavoring material adapted for use in beverages is prepd. by extg. lupulin from hops, treating both the lupulin and hops with ether to ext. oil and the greater part of the soft resin and combing the lupulin and hops after this extn.

13—GENERAL INDUSTRIAL CHEMISTRY

HARLAN S. MINER

The chemical industries in North Carolina. F. C. VILBRANDT. *Ind. Eng. Chem.* (News Ed.) 1, No. 16, 3, 5(1923). E. J. C.

The potentialities of catalytic research in the chemical industry. H. S. TAYLOR. *Ind. Eng. Chem.* 15, 902-4(1923). E. J. C.

Filtration practice. W. WENSE. *Z. angew. Chem.* 36, 310-2(1923); 2 cuts.—The rate of filtration of suspensions is exptly. detd. by means of a graduated tube carrying a disk of filter-stone and fitted into a filter flask. Since the cross-section of the tube and of the disk are identical, the rates are detd. by the distance through which the liquid moves during certain intervals of time. Expts. were carried out with silicic acid suspensions. Totals vols. of filtrate as well as rates are plotted against time, the former being found to decrease very rapidly with time. The rate-time curve leads W. to the following general principle: *A filter may be changed with only so much of a suspension that the filtration is completed before the speed of filtration becomes prohibitively small.* The efficiency of a filter is detd. not only by the actual time required for filtration, but also the time required for cleaning and re-filling. On basis of this fact and also of rate measurements, a table is constructed, from which the optimum height to which a filter should be filled with suspension may be deduced. A discussion is given of the relation between filtration rate and the following: content of solid particles in the suspension; the point where the resistance to filtration increases to the greatest extent; the temp. and viscosity, and H-ion concn. of suspension; effect of pressure greater than atm.; character of filter used; and previous treatments of the suspension. THEO. F. BUEHRER

Graphic study of distilling columns for binary and ternary mixtures. PAUL SAVARIT. *Chimie et industrie Special No.*, 737-56(May, 1923).—S. first takes the case of an ideal column, and then shows how to correct for radiation losses and tray efficiency in actual columns. He applies his findings to the case of the distr. of alc. to 90 and to 95% by vol. resp. (binary mixts.); and to the rectification of alc. to eliminate ethers and fusel oil (ternary mixt.). A. PAFINEAU-COUTURE

Under the sign of industrial economy. GUSTAV GÜNTHER. *Chem.-Ztg.* 47, 573-7, 597-8(1923).—The imperative necessity for economy in industry, as a result of the war, leads to numerous recommendations for the better utilization of water, power, fuel, materials, tools, labor, etc. Both general principles and specific suggestions for attaining this end are offered. W. C. EBAUGH

Preventing segregation of fines in bin discharge. ANON. *Chem. Met. Eng.* 29, 368(1923). E. J. C.

Statistics of industrial accidents in the United States. L. W. CHANEY. U. S. Bur. of Labor Statistics, *Bull.* 339, 60 pp.(1923). E. J. C.

Electrical motors for industrial service. J. L. MCK. YARDLEY. *Ind. Eng. Chem.* 15, 921-5(1923).—A discussion of the application of 60-cycle, a. c., 3-phase motors of standard voltages in the chem. industries. Specifications for special insulation and construction of chem. plant motors are given with a tabulation of suitable methods of arranging the driving system. A. E. MARSHALL

Eliminating stench. W. V. WATSON. *Chem. Met. Eng.* 29, 368(1923).—Pigeon droppings in the seal water of a big gas holder caused an acid condition of the water which led to corrosion. The addn. of lime resulted in a stench due to liberated NH₃. By addn. of 0.1% NaHCO₃ the atm. was effectively sweetened. E. J. C.

Recovering condensable vapors from gases. H. H. ARMSTRONG. U. S. 1,463,782, Aug. 7. Gases such as "casing-head" or natural gases are "reinforced" with the vapor of a low-boiling liquid, e. g., C_2H_2 , C_2H_4 and C_2H_6 , and the gases are expanded in the presence of heavy kerosene, gas oil or other absorbent medium. The low boiling liquid and condensable vapors are sepd. from the absorbent medium and then sepd. from each other by distn.

Heat insulators. Y. KIRI. Brit. 192,659, May 24, 1922. A corrugated sheet is secured to a flat sheet, with the former next to the surface to be insulated; the sheets consist of wire gauze covered with a compn. of MgO , a fibrous material such as asbestos or silicate cotton, and an adhesive material.

Electric resistances. ART.-GRS. KUMMLER & MATTER. Brit. 192,382, Jan. 10, 1923. SiC is heated in Si vapor, produced at about 3,000° by heating a mixt. of quartz and C, to form a resistance material having a small sp. resistance compared with SiC itself. The product, which is very hard, dense, and non-crystalline, will stand very frequent and rapid variations of temp. within wide limits, and will withstand great mechanical strains when in an incandescent state. Bars, plates, etc., of SiC may be subjected to the treatment, which may be varied to form the material in part only. The process may be used for forming the ends of heating bodies of SiC to which terminals are to be fastened.

14—WATER, SEWAGE AND SANITATION

EDWARD BARTOW AND G. C. BAKER

Sulfur, calcium, magnesium and potassium content and reaction of rainfall at different points in Tenn. W. H. MACINTIRE AND J. B. YOUNG. *Soil Science* 15, 205-227 (1923).—The 8 yr. av. of sol. sulfate S precipitations at the University farm was 51.5 lbs. per acre. In the city of Knoxville the av. was 94.5 lbs., while 7 miles from the city only 18.6 lbs. were obtained. Three yr. avs. at 7 other points in the state ranged from 12.7 lbs. in an isolated rural district to 232.4 lbs. near a copper smeltery. Titrations of over 300 samples showed that all were alkaline to methyl orange. Slight acidity to cochineal was observed in two instances. 26.1% of the sol. sulfates could be attributed to Ca, 16.6% to Mg and 30% to K. Only $\frac{1}{2}$ of the acid sol. material in soot was H_2O sol. Rainfall contg. sulfurous material is no more effective in producing acid soils than pure H_2O .

Chemical analysis of the water from wells used by caravans in Arabia. N. GEORGIADIS BRY. *Bull. Inst. Egypte* 5, 63-8(1923).—Chem. analyses are given of samples of water from 7 wells marking the first section of the caravan route from Djeddah to Mecca. Data as to the exact location or geological compn. of the terrain were not available. They are characterized by high nitrate content, high alky., considerable $CaSO_4$, and in several cases by excessive Cl and SO_4 , and cannot be classified as potable.

The occurrence of lead and zinc in the sinter from the hot springs at Nauheim. L. DEBR. *Z. anal. Chem.* 62, 342-8(1923).—Analyses by Will made before 1870 showed the presence of about 3 mg. of As and Zn per kg. of water from the principal springs. Official analyses made between 1903 and 1906 did not show the presence of Zn. In 1914, however, both Zn and Pb were found in the spring water. Some difficulty was encountered in pptg. PbS owing to the presence of so much neutral chloride. Recent analyses made by a somewhat different anal. procedure have confirmed the results obtained before the war and the solids from the water contain about 0.8% ZnO and 0.60% PbO.

Measure of the degree of ionization of mineral waters. ALLYRE, CHASSEVANT AND CHOUCHAK. *Compt. rend.* 176, 1910-13(1923).—The kinds and number of each of the ions present were calcd. from the results of quant. analysis. The mobility of the ions and the equiv. cond. were used in the calcs. in the usual way. The 3 results given varied between 60.82% and 50.22% for the degree of ionization.

Geology and ground water of the Sacramento Valley, Cal. KIRK BRYAN. U. S. Geol. Survey, *Water-Supply Paper* 495, 280 pp., 19 plates(1923).—The physiography, geology and surface waters of the region are described. An examn. of 42 analyses of samples from the northern, western and eastern parts of the valley show no general relation of quality to depth or to geologic formation, neither is there any great variation in the proportions of mineral constituents of the different waters. The engineering problems connected with making wells and with pumping and distributing water are

described. Detailed descriptions of the various areas of the valley, and of their water supplies and logs of wells are given. L. W. RIGGS

Purification of muddy surface water for use in operations at the generating plant of the Deutsches Erdöl A. G. (Berlin). F. H. SCHILLING. *Wasser* 18, 59-60; *Chem. Zentr.* 1922, IV, 621.—*Drainage H₂O from brown-coal mines*, which has been rendered turbid by sand, clay and coal sludge, can be freed from 90% of its suspended material in settling basins and from the remainder by subsequent filtration through sand and made suitable for further use. Should the H₂O still contain humic acid or algae, chlorination of the H₂O must be carried out between the settling basins and the filtration. C. C. DAVIS

The industrial utility of public water supplies in the U. S. W. D. COLLINS. U. S. Geol. Survey, *Water-Supply Paper* 496, 59 pp.(1923).—The public water supplies of 307 cities (not less than 2 samples from each state) are described as to source and treatment, if any, before use. A standard analysis of the mineral constituents of each sample is given. As the utility of a water varies inversely as its hardness, the latter factor is emphasized in this study. The 307 supplies represent about 39 million consumers. Roughly 17 million consumers are served with a water contg. less than 55 parts per million of hardness, 6 million with 55 to 100 parts, 11 million with 100 to 200 parts, and 4.5 million with more than 200 parts. The various methods of treating a municipal water supply to decrease its hardness are described. L. W. RIGGS

Underground contamination of the Bad Axe (Mich.) water supply. W. C. HIRN. *Eng. News-Record* 91, 138-9(1923).—Pollution entered through an unused well 430 ft. from the used well and reached it through fissures opened by dynamiting several years ago. An epidemic of intestinal disorders developed which affected 75% of the population. FRANK BACHMANN

Economics of railway water-supply systems reviewed. C. H. KOVL. *Eng. News-Record* 90, 1091(1923). FRANK BACHMANN

Experiments in water coagulation with aluminum sulfate. F. E. DANIELS. *Eng. News-Record* 91, 93(1923).—With Al₂(SO₄)₃ and Na₂CO₃, max. pptn. occurred at a p_H 6-7. In soln. more alk. than p_H 6.8, dissoln. of the Al₂(OH)₃ began and continued with increasing alky. until the entire floc was redissolved at a p_H of 10.5. Ca aluminates are less sol. than Na aluminates and dissoln. did not begin as soon with the ppt. formed with Ca(OH)₂ as that formed from Na₂CO₃. FRANK BACHMANN

Second water purification plant for Dallas, Texas. DAVID MOREY, JR. *Eng. News-Record* 90, 1042-4(1923).—The city has three sources of supply, artesian wells, Trinity River which is filtered, and the White Rock reservoir, which is filtered in the new plant. The new purification plant is designed for 15 million gal. per day. It consists of a low-lift pumping station, an aerator, a mixing channel, two sedimentation basins, 1 secondary coagulant basin, 12 rapid sand filters, filtered-water reservoir and a wash tank. The aerator is of concrete, 90' x 14' x 7'. The water falls over 8 steps, 86' long so arranged as to give a cascading effect which removes the tastes and odors from the supply. CuSO₄ is used at times in the reservoir to destroy algal growths. From the aerators the water passes through 700' of mixing channels; settled in 2 basins each 300' x 75' x 16'; then to a secondary basin 74.5' x 24' x 13'; and finally to filters. CaO and FeSO₄ are used as primary coagulants and alum in the secondary settling basin. The filters are designed for 2 gal. per sq. ft. of filter area per minute. F. BACHMANN

Disposal of waste water with especial reference to ablation places, laundries and cookhouses. T. S. DUBBING. *J. State Med.* 31, 265-75(1923).—Simplest methods of disposal which are efficient should be used. Where possible underground agricultural drainage should be used after a simple method of purification to remove waste water from the immediate vicinity of the occupied area, and dispose of it on land. Where drainage is not possible wastes should be purified by sedimentation and flotation and passed into pits properly connected in pairs. When soakage pits or disposal areas are likely to be used continuously over long periods and for laundries, some filtration method is necessary to avoid nuisance and to allow absorption of the liquid without clogging. G. C. BAKER

The near future of the waste water problem in the Netherlands. J. C. H. FISCHER. *Chem. Weekblad* 20, 430-1(1923).—Polemical against J. Smit (C. A. 17, 2928). R. BEUTNER

Steel mill installs modern softeners. G. S. REYNOLDS. *Blast Furnace & Steel Plant* 11, 337-9(1923).—A complete system for supplying raw, filtered and zeolite-softened Allegheny River water for the West Penn. Steel Co. plant at Brackenridge, Pa., is described. Water is softened by 2 permutite softeners on intermittent plan, the capacity being adjusted to a period of 8 hrs. between regenerations. Soft water is used

for cooling devices for open-hearth furnaces, on rolls, etc., as well as for boiler feed which requires 480,000 gals. per 24 hrs.

Successful means of removing hard spots from filter beds. W. C. WILLS. *Eng. News-Record* 91, 232-3(1923).—The underdrains consisted of 1 $\frac{1}{4}$ " C. I. laterals on 6" centers and drilled every 6" length with 2 holes, $\frac{1}{4}$ " in diam. Inspection showed that the gravel had cemented above the laterals, stopping the flow of wash water. Tailings in varying sizes 2 x 4 x $\frac{1}{4}$ " to 5 x 6 x 2" substituted for the gravel over the laterals removed the difficulties.

FRANK BACHMANN

Revolving screens for low-lift pumping station, Detroit filters. T. A. LRISEN. *Eng. News-Record* 91, 14(1923).—Seven sets of screens each operated by a 5-h.-p. motor and operating at a speed of 10 ft. per min. are installed in the Detroit water purification plant at a point before the water reaches the pumps. Each screen is made up of 38 panels 24" x 72". The function of the screens is to intercept all floating or slush ice coming through the tunnel and incidentally to prevent passage of fish and floating debris. The openings in the screens are $\frac{1}{4}$ " square.

FRANK BACHMANN

Corrosion detector for boiler feed water control. ANON. *Technique moderne* 15, 440-1(1923).—The app. consists essentially of a chamber divided into two compartments by a highly polished metal disk. The feed water is led into one compartment and steam under boiler pressure into the other. The condition of the disk is examd. after a few mins. and the degree of corrosion is noted.

A. PAINÉAU COÛTEUR

Activated-sludge studies 1920-22. A. M. BUSWELL, *et al.* Ill. State Water Survey, *Bull.* 18, 150 pp.—A description of the sewage expt. station plant of the Ill. State Water Survey is given. The sewage treated was Champaign domestic sewage. **Nitrogen balance.** Analyses of the effluent and influent for free and albuminoid NH₃, nitrate, nitrite, and org. N were made over a period of 63 days; there was a loss of 0.43% of N, which is within exptl. error. There is no volatilization of free NH₃ and no reaction taking place whereby gaseous N is formed; also there is no fixation of atm. N. **Reversal of N cycle and "fixation" of nitrates and NH₃.** The nitrification phase of the activated-sludge process is entirely absent, and nitrification is not essential to the success of the process. Under some conditions clarification and stable effluents may be obtained with so little air that nitrate O in the raw sewage is actually consumed by microorganisms. Max. stability occurs simultaneously with max. air. It is assumed that free NH₃, nitrate and nitrite N are essential foods for the organisms of the sludge. **Wet burning of solids.** Approx. $\frac{2}{3}$ of the solids of the sewage was removed as sludge, the yield being about $\frac{1}{2}$ ton per mil. gals. Sludge analyses showed 99.74% moisture, total solids 2622 p. p. m., total N 211.8 p. p. m., and 5.63% N in the dry sludge. **Relation between vol. and wt. of sludge.** No definite relations existed between the 2 values, and such relations do not furnish good methods of control. **Microbiology of activated sludge.** Activated sludge flocs are of a synthetic gelatinous matrix, similar to that of Nostoc or Merismopedia, in which filamentous and unicellular bacteria are imbedded and on which various protozoa and some metazoa crawl and feed. The purification is accomplished by ingestion and assimilation of the org. matter in the sewage by the organisms, and its resynthesis by them into the living material of the flocs. This process changes org. matter from colloidal and dissolved states to a state in which it will settle out. **Mechanical operation of the plant.** One main feature of the Dorr-Peek tank was that during aeration the sewage and sludge were circulated in a path leading up from the aeration chamber and returned through a centrally located cylindrical well. Another feature was that the settling chamber was placed above and in communication with the aeration chamber thus providing for automatic sludge return, the app. making use of the air-lifting effect of the aerating tank in a tank not complicated by a sedimentation chamber superimposed on the aeration chamber (test runs). **Purification results.** Under good operating conditions the turbidity was reduced from 234 to 48 p. p. m., the O consumed from 58 to 33, nitrates from 2.1 to 0.90. The stability to methylene blue was 43% and the av. bacterial removal was 90-95%. **General operation.** 62,000-93,000 gals. were treated daily, the aerating period being from 7 to 10 hrs. with a variation in the amt. of air used from 0.7 to 1.41 ft.³ When the nitrates of the influent decreased it was necessary to increase the air. **Sludge drying.** Best results were obtained with acidification and sedimentation, and acid heat flotation. Oliver filters, centrifuges and Patterson filters did not give satisfactory results, while the Bailey dryer dried floated sludge, 80-85% moisture, without odor. A bibliography and an appendix of methods, analytical procedures, analyses, etc., are given.

G. C. BAKER

Design features of the Indianapolis activated-sludge plant. C. H. HURD. *Eng. News-Record* 91, 258-62(1923).—Sewage treatment will consist of partial clarification by fine screens and activated-sludge treatment. The plant is designed to treat 50

million gal. per day. The diffuser area is only 7.5% of the tank area. The diffuser plates are set at one side of the tank to give a spiral movement to the liquid. The sewage will have a 6-mile travel through aeration tanks. Settling tanks will treat 1380 gal. per day per sq. ft. of area and during max. flows 2340 gal. with a detention of 97 and 53 min., resp. No definite method of sludge dehydration has been decided upon.

Experience with activated-sludge plant at Eldorado, Kan. A. H. JEWELL. *Eng. News-Record* 90, 1085(1923).—The population increased from 2705 in 1915 to 16,246 in 1918. The old septic tank-chlorination plant was converted into an activated-sludge plant. The remodeling cost \$15,600 as against an estd. cost of tank and trickling filters of \$125,000. The operation cost of the activated-sludge plant was \$5571 in 1921 and \$6735 in 1922. The local authorities have tried to economize in operating cost at expense of character of effluent.

Air-pressure losses in piping of activated-sludge plants. H. L. McMILLAN. *Eng. News-Record* 91, 178-80(1923).

The installation for purification of sewer water at Enschedé. H. G. MOS. *De Ingenieur* 38, 447-9(1923).—A filtering installation according to a German system (Imhoff, Essen) is described.

Sewage effluent as boiler feed water. ANON. *Eng. News-Record* 90, 1049(1923).—If the water is soft, a clarified effluent from a septic tank may be used without treatment. Hard water effluent should be treated with lime and soda to soften and remove org. matter.

Berlin sewage farms in use fifty years. ANON. *Eng. News-Record* 90, 1120(1923).—Irrigation fields for disposal of Berlin's sewage have been in operation since 1873. The vol. of sewage is 132 million gal. per day and the area irrigated 27,000 acres. The land irrigated produces fruit.

Mechanical agitation for sewage activation plant at Wakefield, England. JOHN HAWORTH. *Eng. News-Record* 90, 953(1923).—An activated-sludge plant with paddles instead of compressed air for agitating the sewage is under construction. The plant will consist of screen, grit chamber, settling and aeration tanks, 16 paddle wheels, pumps and final sedimentation tanks.

The role of atmospheric oxygen in the purification of sewage. HANS STOOFF. *Naturwissenschaften* 11, 383-95(1923).—A review is given of the development of the various processes for purifying sewage by aid of atm. O₂ with an extensive survey of the chem. and biol. reactions occurring during the decay of inorg. substances, the fermentation of carbohydrates and the putrefaction of substances contg. N.

Another cross-connection typhoid outbreak. D. C. BOWEN. *Eng. News-Record* 91, 267(1923).—An epidemic was due to a faulty check valve interconnecting industrial with city supply. The industrial supply receives effluent from a septic tank.

A device for water analysis and slow filtration (SIMMONS) 1.

Artificial ice. R. F. LINDSAY. U. S. 1,464,433, Aug. 7. A body of H₂O to be frozen is maintained at substantially constant vol. while carrying off pptd. impurities. The H₂O carrying the impurities is filtered at a temp. of approx. 0°, the filtered H₂O is commingled with air and the aerated H₂O is then injected into the main body of H₂O to agitate it and to replace the pptd. impurities with filtered H₂O from which the ice is in part formed.

Apparatus for softening water. W. PATERSON. U. S. 1,464,291, Aug. 7. The app. is adapted for softening H₂O or purifying it by treatment with reagents such as Al₂(SO₄)₃ soln. or powdered CaCO₃ or Ca(OH)₂, or for treating other liquids with chem. modifying substances. The main flow of liquid to be treated is led through a Venturi tube and a small portion which is led through a by-pass controls automatic intermittent discharge of the reagent used.

15—SOILS, FERTILIZERS AND AGRICULTURAL POISONS

J. J. SKINNER

Manganese, aluminium, and iron ratio as related to soil toxicity. R. H. CARR AND P. H. BREWER. *Ind. Eng. Chem.* 15, 634-7(1923).—In the KCNS method (C. A. 16, 136) for the detn. of soil acidity, a green color appearing in the case of certain soils, after the red of the Fe(CNS)₃, has been discharged by the addn. of a base, has been found

to be due to the presence of considerable amts. of some sol. manganic compd. Analyses of the KCNS exts. of a no. of acid soils showed that the presence of Mn in amts. sufficient to cause the green color is correlated with poor response to liming; other soils, lower in Mn but contg. sol. Fe and Al, were characterized by good response to liming, *i. e.*, after pptn. of the Fe and Al. Since the pptn. of Al and ferric Fe has been shown to be nearly complete at p_H 5.5 and since the Mn pptn. does not commence until p_H 7.2 and is not complete until p_H 7.9, a large excess of base over that required to ppt. the Fe and Al would be necessary to eliminate the Mn. As this excess corresponds to 4 to 5 tons of limestone per acre, it is obvious that attempts to correct for excess Mn in this way would be impracticable aside from the disadvantage of raising the p_H above the optimum 5.5–6.5 (for most crops). Not all unproductiveness of acid soils can be attributed to excess Mn; but it is believed that this element is the chief cause of toxicity in some soils and Al in others. The KCNS method for soil acidity is useful in detecting trouble from these sources.

P. R. DAWSON

Comparison of active aluminium- and hydrogen-ion concentrations of widely separated acid soils. P. S. BURGESS. *Soil Science* 15, 407–12(1923).—Twenty-five samples of acid mineral soils were collected from different sections of the U. S. and Hawaii and their contents of "active" Al detd. by soly. in 0.5 N acetic acid. The p_H values were detd. electrometrically. The correlation between "active" Al and p_H was not very close. Soils more acid than p_H 5 as a rule contained more sol. Al than those less acid. The former group av. 388 p. p. m. sol. Al, the latter group only 26 p. p. m. In general soils showing a high loss on ignition show a high "active" Al content. No relationship was found between the sol. Al and the relative amts. of clay and silt. In general soils from regions of heavy rainfall were higher in sol. Al. With the exception of the Hawaiian laterites the glaciated soils carried more sol. Al than others, the older glaciations contg. more than the latter.

R. BRADFIELD

Variability of nitrates and total nitrogen in soils. A. L. PRINCE. *Soil Science* 15, 395–405(1923).—Variability in soils due to method of sampling was studied, with NO_3 and total N detns. as criteria. Soil from 3 plots receiving different fertilizer treatments was used, 25 samples from each $1/16$ acre plot were analyzed and statistical methods applied to the results. The coeff. of variability ranged from 13 to 42%; the probable error of the mean was 2–5% in the NO_3 detns. Samples low in NO_3 were also low in ability to nitrify $(NH_4)_2SO_4$. The coeff. of variability in the total N studies was only 5.5% and the probable error of the mean only 0.7%.

R. BRADFIELD

The hydrogen-ion concentration of heavy alkaline soils. A. F. JOSEPH and F. J. MARTIN. *J. Agr. Sci.* 13, 321–32(1923).—In connection with the systematic examn. of soils of the Sudan the H-ion concn. of a large no. of soils was detd., and with only 1 exception these were alk., the p_H being always above 8 and sometimes over 9. This communication deals with the methods used and the effect of varying conditions on soil reaction. The electrometric and indicator methods were studied, the method of prep. the soil ext., effect of varying the proportion of H_2O to soil, combined effect of time of extn. and proportion of H_2O upon p_H results are also reported upon. A brief study of the effect of electrolytes and their residual effects upon soil reaction is indicated, as well as the drying of alk. soils. The colorimetric method is unsuited to the examn. of heavy, alk. soils because of the turbidity of the suspension. When the p_H value can be detd. colorimetrically the results agree with the electrometric values. Soil suspensions or moderately clear exts. give results practically identical with those by the electrometric method. Nitrates up to 500 p. p. m. produce no disturbing effects. The period of extn. best suited to these soils is 1 hr. and the proportion of soil to H_2O 1 to 5. The effect of soil on clay is to shift the reaction of acids and alkalis in the direction of neutrality. Na salts displace Al and reduce alky. in soils; and the residual soil after leaching is found to be more alk. The effect of drying these soils is to cause the p_H to be lower than that of the undried soil, but the difference disappears if the time of extn. is prolonged.

R. B. DEEMER

Subsoil acidity. A. P. KELLY. *Science* 58, 36(1923).—From tests of over 500 forest-soil samples there was an increase in acidity with depth to 15 to 30 cm., then a gradual decrease toward neutrality. This was true with the 5 soil types worked with. The variation in acidity with depth was least in the more fertile soil, the Hagerstown loam.

J. J. SKINNER

The acidity of the soil from the viewpoint of its concentration of hydrogen ion. E. A. CARLETON. *Sci. Agr.* 3, 412–4(1923).—A brief popular presentation of the modern conception of soil acidity, its measurement and its practical importance and applications.

P. R. DAWSON

The color of soils in relation to organic matter content. P. E. BROWN and A.

M. O'NEAL. Iowa Agr. Expt. Sta., *Research Bull.* 75, 275-300(1923).—A study of the relation of the color of soils to the N and org. C content indicates that the relationships are only general. Dark color is usually associated with high C and N content, but there is much overlapping when soils of different series are considered. Even in a certain series the relation is not strictly regular. The darker colors are much more satisfactory for comparison, as color comparisons are difficult with light colored soils.

M. S. ANDERSON

Chemical aspects of some North Auckland soils. W. A. GIVEN. *N. Zealand J. Sci. Tech.* 5, 192-6(1922).—The different geological types of soils of the region are briefly described with reference to their phys. and chem. constitution and characteristics, agricultural value and treatment required.

P. R. DAWSON

Titanium in Nile silt. E. GRIFFITHS-JONES. *Analyst* 48, 320-1(1923).—The colorimetric method showed the presence of 1.3-2.55% of TiO₂ in 7 samples of silt from the Nile. In the ash from straw grown on Egyptian soil, 0.4% TiO₂ was detected but no Ti could be found in 10 l. of the river water.

W. T. HALL

Humus in Brazilian coffee soils. MAURICE PIETTRE. *Compt. rend.* 177, 139-41 (1923).—Mech. and chem. analyses are given of 6 virgin soils and the corresponding subsoils before planting to coffee. The humus, as detd. by P.'s pyridine extn. method (cf. *C. A.* 17, 2624), ranged from 0.361 to 13.707% for the surface soils, the higher amts. occurring in the more desirable Sao Paulo lands; the content of the subsoils ranged from 0.325 to 2.08%. The CaO, P₂O₅ and org. N contents of the former were much higher than those of the latter, indicating accumulation of the mineral fertilizing elements in the surface layers where the abundant humus aids their retention. These factors, coupled with the phys. constitution (high clay content) favoring moisture retention, account for the advantages of such soils for coffee culture. The org. and mineral fertility rendered available on clearing should not be destroyed in large part by burning over, as is often the practice, but should be buried in the subsoil by deep working in order to avoid surface oxidation and carrying away during torrential rains and to preserve as completely as possible the abundant reserves so necessary for the long period of culture that the coffee tree demands.

P. R. DAWSON

The shrinkage coefficient of clays and soils. F. HARDY. *J. Agr. Sci.* 13, 243-61 (1923).—A continuation of the researches conducted by others in the British West Indies on the significance of the shrinkage coeff. of clays and soils. The hypothesis which explains shrinkage as due to contraction caused by loss of water by evapp. from the satd. gel-skeleton that ramifies throughout a mass of soil at its point of max. plasticity is criticized. A different hypothesis was sought, and the one finally accepted is based on the belief that colloidal gels possess a reticulated structure. Shrinkage in clays and soils is due to loss of vesicular water. The physical basis of the assumption that the "water content at the point of max. plasticity" represents the inhibition capacity of a clay or soil is discussed in the light of modern theories of plasticity. This const. may provisionally be accepted as marking an important stage in the water relations of clays and soils. Its terminology is open to criticism; alternative titles are suggested.

R. B. DEEMER

The volume changes associated with variations of water content in soil. W. B. HAINES. *J. Agr. Sci.* 13, 296-310(1923).—A new method of measuring the shrinkage of moist soil upon drying is presented. Values for porc space and sp. gr. are detd. at the same time. The character and manner of shrinkage are discussed, and a linear relationship is shown to exist between the shrinkage and moisture content. Tentative explanations are advanced and confirmatory expts. described. The method is used to show the effect of alternate wetting and drying of soil in producing a good tilth.

R. B. DEEMER

Water displacement of soils and the soil solution. J. S. BURD and J. C. MARTIN. *J. Agr. Sci.* 13, 265-95(1923).—The use of a positive air pressure on closely packed soils decreases the time of recovery and increases the yield of soln. by H₂O displacement. Data from 3 sandy loams and 2 silty clay loams indicate that successive displaced solns. of equal elec. cond. were obtained from each soil. The concn. thus measured was in each case the same as that of the liquid obtained without the use of displacing H₂O. Variation in H₂O content of the soil has no effect on the concns. of individual ions. There is, however, an inverse proportion existing between total moisture and concn. of displaced soln. When displaced soil soln. from a portion of soil was substituted for H₂O as the displacing medium upon a second portion of the same soil, this newly displaced soln. had the same concn. as the displacing soln.; this indicates possibly, that this displaced soln. had the same concn. as the soln. with which it came in contact in the soil. Other theoretical aspects of the results are discussed.

R. B. DEEMER

The maximum water-retaining capacity of colloidal soils; the interpretation of this and of certain other soil moisture constants. F. HARY. *J. Agr. Sci.* 13, 340-51 (1923).—The applicability of the Briggs-Shantz relationship connecting max. water-retaining capacity (M) with the hygroscopic coeff. (H) (*i. e.*, $M = 4.3 H + 2$) to soils contg. appreciable amts. of colloidal matter of different specific nature was investigated.

R. B. DREHMER

The soil solution and its importance in the growth of plants. N. M. TULAIKOV. *Soil Science* 15, 229-33(1923).—A brief summary of extensive investigations on the effect of the osmotic pressure of the soil soln. on the growth and chem. compn. of wheat is presented. Increased osmotic pressure retarded the sprouting of seeds, but shortened the period of vegetative growth by 6-7 days. The av. heat, av. wt. of tops and av. yield of grain by wheat plants was slightly greater at 2 atm. than at either higher or lower pressures. The N content of the grains was in some cases increased over 50% by the higher pressures. The hardness of the grain was also increased and the transpiration coeff. decreased at the higher pressures.

R. BRADFELD

Obtaining the soil solution. N. M. TULAIKOV AND M. S. KUZMIN. *Soil Science* 15, 235-9(1923).—A hollow, perforated, brass cylinder is covered with batiste and placed in a definite vol. of soil. The cylinder is evacuated by means of a Karting suction pump. To facilitate the removal of the soln. pressure is applied to the soil surrounding the cylinder by means of screw press; the pressure is gradually increased as the soln. is removed. The authors claim that (1) more of the soln. is obtained by this method than by the older methods, (2) the method is rapid, (3) the soln. obtained is of const. concn. in successive portions, (4) a more concd. soln. may be obtained than in the case of H_2O ext. and (5) quantities of soil varying from 100 g. to 6.7 kg. may be used.

R. BRADFELD

Method for estimating adsorbed bases in soils and the importance of these bases in soil economy. D. J. HISSINK. *Soil Science* 15, 269-76(1923).—When soils are treated with neutral salts the greater part of the reaction takes place within 5 min. The total amt. of adsorbed (replaceable) bases can be estd. by shaking 25 g. of soil with 100 cc. of a warm N soln. of NaCl and allowing the mixt. to settle overnight. The liquid is then poured through a filter into a flask, the mass of the soil brought quantitatively upon the filter and treated with successive portions of the soln. until the flask is filled. A second l. of leachings is obtained in the same way. The difference in content of Ca between the first and second l. taken as a measure of the adsorbed Ca. If the soil contains no $CaCO_3$ the second l. will be practically free from Ca. An av. of the soils examd. contained 30.0 mg. equiv. of Ca, 5.0 of Mg, 0.8 of K, and 2.5 of Na, a total of 38.3 mg. equiv. of replaceable bases in 100 g. of air dry soil. Clay soils ranged from 23.3 to 48.9 mg. equiv., loam soils from 8.4 to 21.8. Normal soils contain about 92 adsorbed bivalent cations to 8 univalent cations. Soils subjected to prolonged leaching by sea water may contain only 50 bivalent cations to 50 univalent cations. This is probably responsible for their poor phys. condition. The adsorbed K was found to be just as available to crops as the H_2O -sol. K. No appreciable exchange is thought to take place between the exchangeable bases and the acid-sol. bases.

R. BRADFELD

Aeration method for determining ammonia in alkali soils. WM. M. GIBBS, RAY E. NEIDIG AND H. W. BATCHELOR. *Soil Science* 15, 261-8(1923).—The MgO method cannot be used for alk. soils because of the splitting off of NH_3 from the soil org. matter. The method proposed is a modification of the method of Potter and Snyder in which the time of aeration is reduced from 15-19 hrs. to 1-1.5 hrs. by keeping the temp. at 75-85°. No NH_3 is split off from the soil org. matter at this temp. 2.6 g. of Na_2CO_3 may be used. The method is reliable for ammonification expts. with alkali soils.

R. BRADFELD

Microbiological analysis of soils as an index of soil fertility. V. Methods for the study of nitrification. S. A. WAKSMAN. *Soil Science* 15, 241-60(1923); cf. *C. A.* 17, 1856.—The rate of nitrification of $(NH_4)_2SO_4$ in soils having different reactions cannot be used as an index of the soils productivity under lab. conditions for the rate of accumulation of NO_3 will depend more on the reaction of the soil and its buffering capacity than on its biol. activities. In this case HNO_3 and H_2SO_4 are formed and a too acid reaction is soon obtained in a poorly buffered soil. In the nitrification of dried blood, NH_3 is first formed and in poorly buffered or slightly alk. media a toxic alky. is soon reached. While no single method is to be relied upon for detg. the nitrifying capacity of a soil, a combination of the following methods is more reliable: (1) nitrification in soln. with 10% of soil for inoculation as recommended by Remy and Lüthms, (2) nitrification of the soils own N, (3) nitrification of $(NH_4)_2SO_4$ in the natural soil, (4) nitrification of $(NH_4)_2SO_4$ in the presence of the theoretical amt. of $CaCO_3$.

necessary to neutralize the acids formed by the oxidation of the $(\text{NH}_4)_2\text{SO}_4$ added, (5) nitrification of org. nitrogenous materials by using low concns. of dried blood (0.1%) and a brief incubation period (10-15 days). By giving a definite wt. to each of these studies a true picture of nitrification in the soil may be obtained.

R. BRADFIELD

Determination of organic matter in decomposition experiments with soil. K. A. BONDORFF AND H. R. CHRISTENSEN. *Soil Science* 15, 361-6(1923).—In detg. mannitol in soil exts. it was found that the reaction did not always follow the equation: $\text{C}_6\text{H}_{14}\text{O}_6 + 13\text{O} = 6\text{CO}_2 + 7\text{H}_2\text{O}$, but that $\text{C}_2\text{H}_4\text{O}_2$ and *n*-butyric acid were sometimes formed. These substances are not readily oxidized by KMnO_4 . An excess of KMnO_4 was required for a quant. oxidation. The following method is recommended. An amt. of aq. ext. corresponding to 0.25 g. soil is treated in a 400-cc. beaker with 50 cc. 0.05 *N* KMnO_4 + 3 cc. of dil. H_2SO_4 (6:100). Heat for 20 min. at 80°, add 50 cc. 0.05 *N* oxalic acid and titrate with 0.02 *N* KMnO_4 .

R. BRADFIELD

Influence of soil condition on bacterial life and changes in soil substance. II. Ability of soil to break down mannitol. H. R. CHRISTENSEN. *Soil Science* 15, 329-60(1923).—See *C. A.* 17, 2467.

R. BRADFIELD

Some preliminary investigations on the relationship of protozoa to soil fertility with special reference to nitrogen fixation. S. M. NASIR. *Ann. Applied Biol.* 10, 122-33 (1923).—The presence of protozoa in the soil does not have a depressing effect upon the nitrogen-fixing bacteria.

C. H. R.

Soil analysis and soil and plant interrelations. D. R. HOAGLAND. California Agr. Expt. Sta., *Circ.* 235, 7 pp.(1922).—The soil minerals enter into soln. at a rate depending on many factors as CO_2 production, temp., moisture, etc. A theoretical discussion is given of the complexity of the soil solns.

J. J. SKINNER

The biochemical sulfur oxidation as a means of improving alkali soils. J. S. JOFFE AND H. C. MCLEAN. *Science* 58, 53-4(1923); cf. *C. A.* 17, 2163.—The work here reported was done to det. the effect of S application on the physical, chem. and biol. structure of alkali soils with a view to its utilization in reclaiming such soils. S oxidizes rapidly in the early period of incubation, and the acid produced coagulates the colloids, destroying the impermeability of the soils and thus allowing leaching operations. There seems to be a possibility of bringing black alkali soils of the most hopeless character back to productivity by S application and leaching. The details are promised in a later publication.

J. J. SKINNER

The so-called "acid soil sickness." O. NOLTE. *Mitt. deut. Landw.-ges.* 38, 369-70(1923).—The yellow color and brown leaf tips sometimes appearing on summer grains and generally believed to be caused by excessive amts. of acid in the soil resulting from the continued use of physiologically acid fertilizer salts such as $(\text{NH}_4)_2\text{SO}_4$ are in reality due to a deficiency of plant food, particularly N. Summer grains affected by this "sickness" are benefited not only by the application of lime marl, lime nitrogen, Thomas meal, and Rhenania phosphate but also by $(\text{NH}_4)_2\text{SO}_4$ and KCl ; NaNO_3 is particularly beneficial. Leguminous plants deriving their N supply from the air are not noticeably susceptible to the action of soils exhibiting a marked deleterious effect upon grains. The p_{H} of "acid sick" soils is frequently identical with that of adjacent unaffected soils.

K. D. JACOB

Effect of adsorption and other factors on certain plant food constituents obtained in the dilute nitric acid digestion of soils and an improvement for their estimation. O. M. SHROD. *Soil Science* 15, 383-93(1923).—The amt. of P_2O_5 , K_2O , CaO and SiO_2 sol. in 0.2 *N* HNO_3 after digesting 5 min. and 5 hrs. was detd. for 73 soils. The 5-min. digestion gave an av. of 91% P_2O_5 , 89% K_2O , 94% CaO and 28% SiO_2 compared to 100% for the 5-hr. digestion in each case. Considerable fluctuation occurred with different soils. The amts. of the above substances extd. varied with the original moisture content of the sample. The addn. of CaCO_3 to the soils in general decreased the amt. of acid-sol. K_2O and increased the acid-sol. P_2O_5 . The acid digestion of short duration is considered of value for comparative studies and for use in connection with soil surveys.

R. BRADFIELD

Recent arrivals on the fertilizer market. LEONHARDS. *Mitt. deut. Landw.-ges.* 38, 398-400(1923).—So-called "humus prepn." such as "Humus silicic acid," "Humus carboineum," "Peat lime," "Guanol," and "Biohumus" possess little or no fertilizing value other than their content of available N, P_2O_5 , K_2O or CaO ; this is also true of such lime fertilizers as "End-liquor lime" and "Sulfate-lime." The source, compn., and prepn. of these materials are discussed.

K. D. JACOB

Some features of design and operation in a modern fertilizer plant. CHARLES WADSWORTH, 3RD. *Chem. Met. Eng.* 29, 179-83(1923).—An illus. description of the

large acid phosphate plant of the Davison Chem. Co. at Curtis Bay, Md. It deals principally with the handling of the raw materials, and the manuf. of H_2SO_4 by the chamber process. Outstanding points are: the well planned layout, the labor-saving devices, the size of the hot tower and the means of boosting the burner gases to the hot tower. The tower is 30 ft. (9.15 m.) in diam. and working at capacity will keep 2 cold towers busy absorbing niter gases. Wedge, Herreshof pyrite burners and rotary sulfur burners are available.

W. H. BOYNTON

Large scale production of acid phosphate at the Davison Chemical Company's plant. CHARLES WADSWORTH, 3RD. *Chem. Met. Eng.* 29, 265-70 (1923); cf. preceding abstr.—This instalment deals with the production and handling of the acid phosphate.

W. H. BOYNTON

Reversion of acid phosphate in acid soils. T. D. HALL AND J. C. VOGEL. *Soil Science* 15, 367-9 (1923).—Acid phosphate with and without $CaCO_3$ was mixed with two acid soils and the 2% citric acid sol. P_2O_5 detd. after 30 days. No significant differences were obtained with different orders of mixing the lime, phosphate and soil. One soil inverted 24.46-31.68% of the P_2O_5 in 30 days, the other 59.72-62.43%. The former contained 1.58% Fe_2O_3 and 1.65% Al_2O_3 , the latter 5.67% Fe_2O_3 and 9.79% Al_2O_3 .

R. BRADFELD

Availability of adsorbed phosphorus. R. C. WILEY AND N. E. GORDON. *Soil Science* 15, 371-3 (1923).—Colloidal Fe_2O_3 and Al_2O_3 were allowed to reach equil. in a 0.05 N KH_2PO_4 soln., then washed with dist. H_2O until the washings showed no test for P_2O_5 . The gels still contained about $1/3$ of the original P_2O_5 . They were mixed with sand, treated with a P_2O_5 -free nutrient soln. and a sweet potato seedling was planted in each. The plants receiving the adsorbed, unleachable P_2O_5 made a good growth and showed a gain in P_2O_5 content. Plants receiving sol. P_2O_5 in addition to the adsorbed P_2O_5 made a more rapid growth. The plants treated with the Fe_2O_3 gel contained more P_2O_5 than those treated with the Al_2O_3 gel.

R. BRADFELD

Contribution to the knowledge of the action of phosphoric acid fertilizers. GERLACH AND O. NOLTE. *Mitt. deut. Landw.-ges.* 38, 259-64 (1923).—The authors do not agree with the theory of Aereboe (C. A. 17, 1104) that the use of heavy applications of physiologically acid fertilizer salts such as $(NH_4)_2SO_4$ and concd. K salts renders available the insol. P_2O_5 present in the soil and eliminates the necessity of P_2O_5 fertilizers. The work of other investigators is reviewed and the results obtained by the authors during 1922 are tabulated. Winter rye, winter wheat, potatoes, barley, and meadow receiving basic applications of $(NH_4)_2SO_4$ and concd. K salts responded favorably to applications of P_2O_5 in the form of Thomas meal, Rhenania phosphate or superphosphate. With winter rye Thomas meal gave somewhat better results than did an equiv. amt. of Rhenania phosphate. With winter wheat Thomas meal was more beneficial on medium loam soil and Rhenania phosphate on sandy loam. With potatoes superphosphate gave the greatest increases over the basic fertilizers on new sandy loam and the lowest on sand soil. The greatest increases were in general obtained with the largest applications of superphosphate.

K. D. JACOB

Fertilizing cultivated plants with sulfur. O. NOLTE AND R. LEONHARDS. *Mitt. deut. Landw.-ges.* 38, 248-9 (1923).—The results of a no. of pot and field expts. with S on lucern and other fabaceous plants did not in general show any significant increases in yield over the check expts. In some cases S apparently exerted a pronounced favorable action but the results were not concordant for any one series of expts. S did not significantly increase the amt. of inorg. constituents of lucern nor the yield nor starch content of potatoes.

K. D. JACOB

The efficiency of ammonium sulfate as a fertilizer. J. A. PRESCOTT. *J. Agr. Sci.* 13, 333-9 (1923).—Field expts. with maize at the Bahaim Exptl. Sta. and lab. tests indicate that the lower efficiency of $(NH_4)_2SO_4$ as compared with $NaNO_3$ is due principally under these special conditions to the liberation of NH_3 from the fertilizer in contact with the alk. soil. The rate of this liberation is a function of the aeration and of the soil reaction.

R. B. DEEMER

A comparison of magnesian and non-magnesian limestone in some five-year rotations. J. G. LIPMAN, A. N. BLAIR, H. C. MCLEAN AND A. L. PRINCE. *Soil Science* 15, 307-28 (1923).—Magnesian and non-magnesian limestones have been applied to four different 5-yr. crop rotations for 15 yrs. at the rates of $1/2$, 1 and 2 tons per acre on a soil having an initial lime requirement of 1000-1500 lbs. per acre. Legume crops were included in every rotation and 300-400 lbs. of acid phosphate, 100-200 lbs. of potash and commercial nitrogenous fertilizers equiv. to 100-200 lbs. $NaNO_3$ have been added. No farm manure was used. Nearly all limed plots have shown substantial increases in yield over the checks. The 1-ton application proved as effective in most cases as the

2-ton. In a few cases there was evidence of injury with 2 tons of magnesian limestone; as a whole, however, the $MgCO_3$ was slightly superior to the $CaCO_3$. The N content of the crops was higher in the limed plots and that of the $MgCO_3$ plots higher than that of the $CaCO_3$ plots. The N content of the soil has been fairly const. for the last 10-yr. period with a slight increase. The expt. indicates that it is not necessary fully to satisfy the lime requirement of the soil as commonly detd. in order to get good results with most farm crops. R. BRADFELD

Solubility of limestones as related to their physical properties. M. F. MORGAN AND R. M. SALTER. *Soil Science* 15, 293-305(1923).—Twelve limestones of widely varying chem. and physical properties were tested for porosity, hardness, sp. gr., cryst. compn., chem. analysis, and rate of soly. There was no apparent relationship found between any of the physical properties studied and rate of soly. The samples contg. considerable $MgCO_3$ were more slowly sol. than the more highly calcic stones. With 100-mesh material the rate of soly. of even the dolomitic material is believed to be sufficiently rapid for all practical purposes. R. BRADFELD

What is the future of the mixed fertilizers? F. E. BEAR. *Chem. Met. Eng.* 28, 1121-2(1923).—In expts. conducted at Wooster NaN_3 proved more beneficial to corn, oats, wheat, clover and timothy than did oil meal, dried blood or $(NH_4)_2SO_4$. A discussion of high-analysis mixts. is given. J. J. SKINNER

The value of lime and inoculation for alfalfa and clover on acid soils. E. J. CRAUL AND E. B. FRED. Iowa Agr. Expt. Sta., *Research Bull.* 54, 22 pp.(1922).—Results of field and greenhouse studies show that alfalfa and clover on acid soils grow best when nodule bacteria are added and the acidity of the soil is neutralized by liming. J. J. SKINNER

Chemistry in the control of plant enemies. New achievements and future possibilities. W. C. O'KANE. *Ind. Eng. Chem.* 15, 911-3(1923).—The uses of various chemicals for controlling insects and plant diseases are discussed. Among the subjects given consideration are the effect of *p*-dichlorobenzene on peach borers, S sprays for plant diseases, NaF for roach destruction and CS_2 for mosquito control. J. J. SKINNER

Pyrethrum and vine worms. A. DUFOUX. *Rev. vit.* 59, 99-101(1923).—A discussion of the effectiveness of the insecticide and its application. P. R. D.

The triumph of copper. FONZES-DIAON. *Prog. agr. vit.* 80, 88-9(1923).—Attempts to explain the activity of Bordeaux and Burgundy mixts. on the basis of other constituents than Cu and to substitute sprays not contg. Cu have met with failure in practice. The position of Cu as an indispensable factor in anti-mildew sprays is vindicated. P. R. DAWSON

Powdered Bordeaux mixture. R. H. ROBINSON. *Ind. Eng. Chem.* 15, 941-2(1923).—A method is suggested for the prepn. of Bordeaux mixt. in which powdered $CaSO_4$ and $Ca(OH)_2$ are used in the dry form. Recommendations for a commercial prepn. are as follows: Fill the spray tank with 50 gallons of water. After starting the agitator add 4 lbs. $CuSO_4$. Then sift into the tank 4 lbs. hydrated lime plus 0.01% of casein. The Bordeaux mixt. is then ready for spraying. J. J. SKINNER

Notes on the control of "cutworms" by poisoned bait. J. C. F. FRYER AND R. STENTON. *Ann. Applied Biol.* 10, 241-52(1923).—A poisoned bran bait was effective for the control of cutworms in mangold and swede fields. Lab. expts. failed to produce anything better than moist bran; the addn. of essential oils, molasses, lemon juice, amyl acetate and a number of other substances did not increase the attractiveness of the bran. Cutworms chose moist bran as often as they did their natural food. Methods of experimentation are given. CHAS. H. RICHARDSON

Sulfur, calcium, magnesium and potassium content and reaction of rainfall (MACINTIRE, YOUNG) 14.

Fertilizers. E. I. PEASE. *Brit.* 192,778, Nov. 8, 1921. Peat, powd. coke or coal, or a mixt. of these substances or peat mixed with clay, shale, sand or soil, is impregnated with H_3PO_4 , with or without H_2SO_4 , and the product utilized for absorbing NH_3 . H_3PO_4 , obtained by treating phosphate rock with H_2SO_4 and sepg. the $CaSO_4$ formed, may be used. The treatment of the base material with NH_3 may be carried out in the cold and prolonged to secure the formation of $(NH_4)_3PO_4$. Cf. C. A. 17, 3071.

Fertilizers. L. D. POOCK. *Brit.* 192,835, May 18, 1922. A liquid fertilizer is obtained by steeping finely divided deciduous leaves in hot water, allowing the mixt. to cool, fermenting it with yeast or other agent, and draining off the liquid from the leaves. A preservative such as $BzONa$ is added to the liquid. A fertilizer for use as a mulch is

obtained by adding to the residual leaves as much of the liquid fertilizer as they will absorb. Cf. C. A. 17, 848.

Granulating lime nitrogen. S. E. ROOLING and A. P. ZAMORE, *Can.* 233,344, Aug. 7, 1923. Pulverulent CaCN_2 is treated in a container, through which it is conveyed with dil. HNO_3 and agitated to granulate and dry it. The container may be heated and the CaCN_2 may be also treated with an oil.

Insecticides, fungicides, and preservatives. A. MAL, *Brit.* 191,793, Oct. 11, 1921. Insecticides, fungicides, and preservatives for wood and for spraying plants are prepd. by treating arsenic compds. which are not normally sol. in org. solvents with halogens or with inorg. or org. halogen-yielding compds. in order to render them sol. in org. solvents. The As compds. specified are As acids, sulfides of As, and Paris green. Br is a suitable halogen and AsBr₃, AsCl₃, phthalyl chloride, $\text{CBr}_3\text{CO}_2\text{H}$, and $\text{C}_6\text{H}_5\text{Cl}$ are suitable halogen-yielding substances. Solvents specified are acetone, ethers, alc., amyl acetate, Et(OAc), benzene, toluene, tar oils, and petroleum. For spraying plants, the solns. may be dild. with H_2O , and slaked lime added to neutralize any free acid. Known insecticidal compds. contg. arsenical compd. and tar oils, and paints and varnishes contg. As chemically bound by condensation products of phenols and HCHO are also referred to. Cf. C. A. 17, 2469.

16—THE FERMENTATION INDUSTRIES

C. N. FREY

Mechanism of the action of malt amylase. H. LÜERS and W. WASMUND, *Z. ges. Brauwesen* 45, 81-5, 127-30, 133-7, 144-6, 147-50, 152-4 (1922); *Chimie et industrie* 10, 148 (1923); cf. C. A. 16, 3098. - Saccharification does not take place according to the law of monomol. reactions, and hence the rate of saccharification is not proportional to the amt. of unhydrolyzed starch. The reaction const., K , calcd. according to the log-arithmetic law of monomol. reactions, increases as saccharification proceeds until about 80% of the starch has been hydrolyzed and then decreases. The character of the hydrolysis remains the same whatever the relative proportions of substrate and of enzyme, the quality of the starch, and the reaction of the medium within the prescribed limits (p_{H} 4.28-6.69). The amt. of sugar formed is approx. proportional to the time up to the destruction of about 40% of the starch, but thereafter hydrolysis no longer follows the law of monomol. reactions. With enzyme concn. of 0.005-0.05% and initial starch concn. of 0.75-6% the reaction const. during the first phase of hydrolysis is inversely proportional to the starch concn. With a 3% starch concn. and amylase concn. of 0-0.1% the rate of saccharification is approx. proportional to the enzyme concn. until 30-40% of the starch has been destroyed, which confirms Kjeldahl's well known "law of proportionality." In saccharification of a 3% starch soln. with 0.05% of amylase the reaction const. at the beginning is 1.506 times greater at 50° than at 40°, 1.688 times greater at 40° than at 30°, and 1.89 times greater at 30° than at 20°. Addn. of 0.5% of maltose to a 3% soln. of starch contg. 0.05% amylase reduces the rate of saccharification 6.34%. Larger quantities of maltose have a more marked effect. The retarding effect of achrödextrin is greater than that of an equiv. amt. of maltose. Considerable differences were noted in the rate of hydrolysis of different starches, e. g., Lintner sol. starch, the same previously heated in an autoclave, Malfitano starch, starch degraded according to Maquenne, and potato starch. Variations in reaction within certain limits affect the rate but not the general character of the hydrolysis. Heating at 60° for 13 min. reduces the activity of amylase soln. of optimum reaction to the extent of about 50%, and to a greater extent at other reactions. A. P.-C.

Yeast. INTERNATIONAL YEAST CO., LTD. *Brit.* 192,085, Jan. 18, 1923. Nutrient liquids for cultivating yeast by an aeration process contain a proportion of EtOH up to 1.5-2% of the vol. of the liquid. The yeast may be cultivated in a wort prepd. as described in 13,193, 1913 (C. A. 8, 3835) by soaring an ordinary grain mash with lactic acid bacteria and neutralizing with NH_3 , and 10% of 25 proof alc., added after 4 hrs. fermentation, or the alc. may be added at the beginning of the fermentation. Cf. 155,281.

17—PHARMACEUTICAL CHEMISTRY

W. O. EMERY

Detection of quinine in the presence of antipyrine or pyramidone. DOMENICO GANASSINI. *Boll. chim. farm.* 62, 321-2(1923).—Antipyrine and pyramidone interfere with the usual tests for quinine. If Cl water and then NH_4OH are added to the mixt. a fine rose or red color appears, then a red ppt. The name *quinerythropyrine* is proposed for the red coloring matter. The reaction is more delicate when the quinine and antipyrine (or pyramidone) are present in equal parts.

The determination of santonin in flores cinæ (wormseed). L. M. VAN DEN BERG. *Pharm. Weekblad* 60, 858-70(1923).—The following modified method is recommended. Heat 5 g. of wormseed with 30 cc. of H_2O in a steam bath for 15 min., add 10 cc. of dil. HCl and heat 15 min. as before. After cooling add 60 cc. of CHCl_3 , shake vigorously for 5 min., add 5 g. of tragacanth and shake again until the CHCl_3 seps. Filter off 40 cc. of the CHCl_3 through a small filter. Distil off the CHCl_3 and boil the residue 15 min. with 50 cc. of 15% EtOH, avoiding loss by evapn. Filter while still hot, wash twice with 10 cc. of boiling 15% EtOH and collect the filtrate in a tared flask. Allow the filtrate to stand 24 hrs. in a cool place. Weigh the flask and contents and filter on a small tared filter, rinsing twice with 10 cc. of 15% EtOH. Dry the flask and filter at $100-5^\circ$. Add to the wt. of the santonin 6 mg. for every 10 g. of solvent contained in the flask immediately before filtering.

Physiological standardization. J. S. WHITE. *Analyst* 48, 303-14(1923).—A discussion of the gradual development of this science, and of expts. tending to show how it is possible to det. with fair accuracy the proper dosage of such drugs as are not amenable to chem. assay, or where chem. standardization is inadequate. Among the drugs deserving of consideration in this respect are aconite root, belladonna leaf and root, Russian cantharides, red cinchona, coca leaf, digitalis, ergot, gelsemium, hyoscyamus, hydrastis, ipecac, jalap, mandrake, nux vomica, gum opium, sanguinaria, stramonium leaf. Exptl. findings are reported for digitalis, strophanthus, ergot and an anti-diphtheria serum.

Replacement of Bettendorf's reagent by hydrochloric acid and calcium hypophosphite solution. E. RUPP AND E. MUSCHOL. *Ber. pharm. Ges.* 33, 62-4(1923).—Instead of the Na salt employed by Atterberg (cf. *Chem.-Ztg.* 264(1901) and Bougault (cf. *Ibid* 1902, Rep. 175), R. and M. recommend the officinal $\text{Ca}_3(\text{PO}_3)_2$ dissolved in 10 parts of HCl (1.126). Just as with Bettendorf's reagent, tests were applied to the various pharmacopœial products, previously adulterated with 0.1 to 1 mg. of As_2O_3 , by the addition of several cc. of the reagent to the sample in a test-tube immersed in boiling H_2O for 30 min. In expts. with dil. HCl, H_2SO_4 , AcOH and MgSO_4 , a distinct browning of the liquid was observable after 20 min. Many other examples are cited showing the usefulness of this reagent.

Bactericidal action of mercury oxycyanide. O. ТОМЦЕК AND M. КРЕДБА. *Chem.-Ztg.* 47, 489-90(1923).—The bactericidal action of mercuric cyanide in aq. solns. is less than that of HgCl_2 , being practically identical in the pure form $\text{Hg}(\text{CN})_2 \cdot \text{HgO}$ and in the com. product $3\text{Hg}(\text{CN})_2 \cdot \text{HgO}$. In the preps. less basic than the latter the bactericidal strength suffers diminution, finally reaching its minimum in $\text{Hg}(\text{CN})_2$. Rise in temp. within limits favorable to microbial development is followed by an increase in the bactericidal action of mercury oxycyanide preps. In solns. contg. proteins (peptone, serum albumin), the bactericidal action falls as in the case of HgCl_2 , although the mercury oxycyanide-protein compds. are more sol. in protein excess than those of HgCl_2 . The action of HgCl_2 is even under these conditions superior to that of oxycyanide. The alkali metal tartrates and acetates, ordinarily present as constituents of mercuric oxycyanide tablets, are without any practical effect on the bactericidal action of the Hg compds. On the other hand, the addition of other alkali metal salts in sufficient quantity not only prevents the formation of protein ppts. but also effects a very marked increase in the bactericidal action of both $\text{Hg}(\text{CN})_2 \cdot \text{HgO}$ and HgCl_2 . For practical purposes disinfection is best carried out with 2% luke-warm aq. solns. of $\text{Hg}(\text{CN})_2 \cdot \text{HgO}$.

Estimation of easily dehydrated alcohols in essential oils. L. S. ГЛАУТЧ. *Compt. rend.* 177, 268-70(1923).—Ordinarily the free alcs. of essential oils are estd. by acetylation with Ac_2O and titration of the esters thus formed. In the method outlined below esterification is effected by the aceto-formic anhydride of Behal (cf. *Bull. soc. chim.* [3], 23, 745(1900)), prepd. by pouring 1 part of HCO_2H ($d_{20} 1.22$) into 2 parts of Ac_2O (100%), free from Cl, and kept at a temp. not exceeding 15° , then gradually warming to

50°, at which point it is suddenly cooled. Place 15 cc. of this mixt. in a 30-cc. bottle, add 10 cc. linalool or the sample in question, mix well, cork tightly and immerse the bottle in ice H₂O, finally allowing it to stand at about 20° during 72 to 96 hrs. An excess of the reagent or prolongation of the reaction causes no material change in the result. Any less quantity of the formylating mixt., however, is insufficient in the case of pure linalool. At the end of the specified time, the unexpended anhydrides are digested for 2 hrs. in the cold with 50 cc. H₂O, the mixt. is then washed with H₂O, a 5% soln. of NaHCO₃, and finally twice again with H₂O. Dry over anhydrous Na₂SO₄, hydrolyze in the usual way, heating 1.5 hrs. to boiling in order completely to saponify small amts. of terpenylic esters formed by isomerization. Calc. the amt. of alc. according to the Schimmel formula: $A\% = nM/10(p - 0.028n)$, in which n represents the no. of cc. of N KOH used in saponifying p g. of formylated product, and M the mol. wt. of the alc. estd. G. shows by several examples the superiority of the present method over those ordinarily employed, notably in the case of essential oils having linalool as a constituent.

W. O. E.

Alkaloids. A. R. BLISS, JR. *J. Assoc. Official Agr. Chem.* 7, 1-3(1923); cf. *C. A.* 16, 3167.—Two assays are recorded, one of stramonium ointment, the other of belladonna ointment, and the method is described for their treatment collaboratively. A report of the collaborative findings is postponed. Recommendations are made: that B.'s method for the sepn. of quinine and strychnine, Ewe's method for the assay of physostigma and its preps., and Fuller's method for assaying hyoscyamus be adopted as official; that B.'s method for assaying stramonium ointment, Ewe's method for assaying belladonna ointment, and Ewe's method for the assay of belladonna liniment be submitted to collaborative study; that methods for detg. atropine in tablets, and assaying ipecac and its preps. be studied.

W. O. E.

Separation of cinchona alkaloids. E. O. EATON. *J. Assoc. Official Agr. Chem.* 7, 4-5(1923); cf. *C. A.* 16, 3168.—It is recommended that the methods for quinidine and other cinchona alkaloids be further studied.

W. O. E.

Methods of analysis of morphine, codeine and diacetylmorphine. C. K. GAYCARR. *J. Assoc. Official Agr. Chem.* 7, 6(1923); cf. *C. A.* 16, 1636, 3167.—In view of the results obtained in collaborative studies, it is recommended that the methods of analysis for morphine, codeine and diacetylmorphine be adopted as official.

W. O. E.

Laxative and bitter tonic drugs. H. C. FULLER. *J. Assoc. Official Agr. Chem.* 7, 7-10(1923); cf. *C. A.* 16, 3167.—Methods of examn. are given, as also the collaborative results obtained in expts. with cascara sagrada and aloin. It is recommended that the work on such drugs be continued.

W. O. E.

Acetylsalicylic acid. A. E. PAUL. *J. Assoc. Official Agr. Chem.* 7, 10 3(1923); cf. *C. A.* 16, 3167.—As the result of collaborative studies on the melting point, and methods for estg. free and total AcOH in acetylsalicylic acid, it is recommended that the methods outlined be subjected to further study; that Eaton's idea of detg. the melting point before and after crystn. from hot CHCl₃ be examd. on pure and impure samples; that the problem of detg. aspirin in the presence of possibly interfering substances be given consideration.

W. O. E.

Determination of phenolphthalein. SAMUEL PALKIN. *J. Assoc. Official Agr. Chem.* 7, 14-7(1923).—Methods are outlined and results obtained in collaborative studies given. In view of certain inconsistencies shown in the results, further study is recommended to det. the possible sources of error.

W. O. E.

Qualitative and quantitative methods for the examination of procaine (novocaine). A. W. HANSON. *J. Assoc. Official Agr. Chem.* 7, 17-20(1923); cf. *C. A.* 16, 1636, 3168.—The results obtained during this and the past year show that the bromide-bromate method is the more accurate, being especially useful in indicating whether all the substance assayed is procaine. In cases where it is necessary to ext. the base the residue can be converted into the HCl salt in the manner previously described. It is recommended that the tests and method (bromide-bromate) presented at the last 2 meetings be adopted as official; that the extn. and titration method submitted at the last meeting be adopted as official.

W. O. E.

Examination of medicinal methylene blue. H. O. MORAW. *J. Assoc. Official Agr. Chem.* 7, 20-9(1923).—The method proposed and tried out collaboratively is based upon expts. suggested by methods on the use of methylene blue in I titrations instead of starch, by Sinnatt (*C. A.* 4, 3054). The principles employed in the proposed method for the extn. of methylene blue and its removal from the solvent by diln. with CCl₄ are substantially the same as those used by Mathewson (*C. A.* 11, 3341). The results obtained were such that the recommendation is made to adopt the method tentatively and subject it collaboratively during 1923.

W. O. E.

Qualitative and quantitative methods for the determination of pyramidone. A. W. HANSON. *J. Assoc. Official Agr. Chem.* **7**, 29-32(1923).—Following the description of qual. tests for differentiating pyramidone from antipyrine, methods are outlined for the isolation and estn. of pyramidone as such or its hydrochloride, the latter by weight or titration with standard alkali. It is recommended that the extn. method, as also that for estg. the hydrochloride, be studied during the present year. W. O. E.

Phenylcinchoninic acid (cinchophen, atophan). WM. RABAK. *J. Assoc. Official Agr. Chem.* **7**, 32-4(1923).—A method is proposed for estg. the substance by treating in abs. EtOH (1 g. of the powdered sample dissolved in boiling EtOH) with 50 cc. of 0.1 N NaOH in the presence of phenolphthalein, and titrating the excess alkali with 0.1 N acid. Each cc. of 0.1 N alkali expended corresponds to 24.91 mg. of phenylcinchoninic acid. W. O. E.

Chloramine-T. W. H. HEATH. *J. Assoc. Official Agr. Chem.* **7**, 34-6(1923).—Tests for identity and purity are described as also methods for estg. the available Cl. Recommendation is made that chloramine products be subjected to collaborative study. W. O. E.

Eucalyptus cneorifolia rectification residues. ANON. *Perfumery Essent. Oil Record* **14**, 175-7(1923).—The sample, an almost black mobile oil, consisted of phenol (australol) over 6%, and aromatic aldehydes (principally cryptal) 25%, the remainder being sesquiterpenes, alcohols, products resulting from polymerization, as well as colloidal Fe compds. derived from the still. The crude oil emulsified with a neutral soap gives a coeff. comparable to the tar oil products on the market. W. O. E.

Determination of phenols and aldehydes by absorption methods. C. E. SAGE. *Perfumery Essent. Oil Record* **14**, 178-9(1923); cf. W. H. Simmons, *C. A.* **16**, 613; Bennett and Garratt, *C. A.* **17**, 2629.—The published figures show that the alkali dissolves some of the terpenes as well as the phenols. It therefore seems desirable either to make a correction for this soly. or to standardize the flask and its size, particularly the latter factor. The lack of uniformity in the pharmacopeial procedure explains why control chemists in various parts of the world do not always agree within 1%. W. O. E.

Solubility test for Ceylon citronella oil. M. S. SALAMON. *Perfumery Essent. Oil Record* **14**, 179(1923).—It is shown that in the instructions given on London contracts no observation of the soln. is to be made until 10 vols. of alc. have been added. This is a very important departure from the Schimmel procedure, since there are many samples of Ceylon citronella oil which, after giving a bright soln. in 2 vols. of 80% alc., will give a decidedly turbid soln. with about 4 vols., and then a bright or only a slightly opalescent soln. when as much as 10 vols. have been added. While acceptable in London, it is doubtful whether Schimmel would so regard such oils. W. O. E.

Characters and evaluation of Italian bergamot oil of the 1922-3 season. ANON. *Perfumery Essent. Oil Record* **14**, 180(1923).—On account of an abnormally dry season certain properties of bergamot oil showed appreciable differences from the normal in 1920-1. These became normal again the following year. The effect of the prolonged dryness from spring to autumn of 1922 is now examd. Detailed analytical figures for 47 samples from 36 different districts are tabulated, of which the following is a summary, the highest, lowest and av. being mentioned in the order named: d_{15} 0.8694, 0.8797, 0.8846; $[\alpha]_{D}^{20}$ 32° 12', 11° 24', 19° 48'; ester as linalyl acetate 49.80, 33.11, 40.73%; sapon. no. 137.5, 96.0, 117.7; acid no. 1.90, 0.70, 1.26; residue non-volatile on H₂O bath 6.38, 4.43, 5.44%; sapon. no. of residue 191.6, 145.0, 171.7; free alc. calcd. as linalool 8.44, 0.70, 4.26%; combined alc. as linalool 39.09, 27.66, 31.93%; total alc. as linalool 40.13, 28.73, 36.20%; aldehyde as citral 1.68, 0.80, 1.20%; total oxygenated compds. (esters, aldehydes and alcs.) 51.71, 37.39, 46.19%. Other values given in the article show that the $[\alpha]$ of a bergamot oil is no criterion of its content of substances useful in perfumery. W. O. E.

Estimation of chloral hydrate. E. RUPP. *Pharm. Zentralhalle* **64**, 151(1923).—In the iodometric estn. of CCl₃CH(OH)₂, it is essential that the I soln. be added before the alkali. Ten cc. of 0.1% CCl₃CH(OH)₂ soln. is treated with 25 cc. of 0.1 N I soln. and 2.5 cc. of N NaOH soln. After 10 min. the mixt. is acidified and the excess of iodine titrated with Na₂S₂O₄ soln. W. O. E.

History of modern salve technic. I. LIFSCHÜTZ. *Pharm. Zentralhalle* **64**, 305-8 (1923).—A discussion of various salve bases involving notably vaseline and the hydrophil constituents of lanolin. W. O. E.

Biological evaluation of drugs. F. F. WERNER. *Pharm. Ztg.* **68**, 493-5(1923).—A plea for the more extended use of biol. methods, notably by pharmacists, including various procedures for testing cocaine, K-strophanthin, atropine, suprarenin, santonin, CCl₃CH(OH)₂, Fowler's soln. and caffeine. W. O. E.

Testing caffeine-sodium salicylate. BOHRISCH. *Pharm. Zentralhalle* **64**, 363-5 (1923).—Consideration is given to the tendency of this product and Na salicylate as well to develop colored solns. particularly on standing. Such coloring arises largely from a condition of alkalinity in the product itself, which should, in order to insure greater stability in soln., possess a slight excess of salicylic acid. W. O. E.

Use of blood fibrin in the preparation of iron albuminate solution. D. SCHENK. *Pharm. Ztg.* **68**, 534-5 (1923).—Directions are given in detail for prep. this soln. W. O. E.

Commercial silver nucleates. C. MANNICH AND K. RITSERT. *Pharm. Ztg.* **69**, 587 (1923).—One sample (Boehringer) yielded on analysis the following data: H₂O loss over H₂SO₄ 9.7, ash (Ag and P₂O₅) 30, Ag 13, N 13.2, and P 6.81%. Atomic ratio of N:P = 3:12.9. Yeast nucleic acid calls for the ratio 3P:13P. A second sample (Hockert and Michalowsky) showed H₂O loss of 9.8 and ash 37%, in which latter Ag, K, traces of Cl and P₂O₅ were present. Ag content 20.7, N 8%. The absence of determinable P in this sample indicated that only the merest traces of nucleic acid could be present. The product was most likely one of the numerous Ag proteinates. W. O. E.

Potassium ferrocyanide as a reagent in the microscopic qualitative chemical analysis of the common alkaloids. H. I. COLLE. *Philippine J. Sci.* **23**, 97-101 (1923).—Thirteen of the common alkaloids (aconitine, apomorphine, arecoline, atropine, berberine, β -eucaine, brucine, caffeine, cinchonidine, cinchonine, cocaine, codeine, conine, curare, emetine, ergotinine, heroine, homatropine, hydrastine, hyoscyamine, morphine, marceine, narcotine, nicotine, novocaine, papaverine, physostigmine, pilocarpine, piperazine, piperidine, piperine, quinine, quinoline, scopolamine, sparteine, stovaine, strychnine, theobromine, theophylline, veratrine) yield cryst. ppts. with K₄Fe(CN)₆ in HCl soln., sufficiently characteristic to be used as corroborative identification tests. These tests can be applied to very minute amts. of material. K₄Fe(CN)₆ is a satisfactory microchem. reagent for the distinction of cinchonidine, cinchonine, and quinine. Brucine and strychnine are readily distinguished by this reagent. Cocaine can be distinguished from β -eucaine, stovaine, and heroine by the K₄Fe(CN)₆ test. The sensitivity of the K₄Fe(CN)₆ test for the various alkaloids has been detd. Crystals of some 12 alkaloids are shown in photographic reproduction. W. O. E.

Revision of the German Pharmacopoeia. THEODOR PAUL. *Z. angew. Chem.* **36**, 345-8 (1923).—In discussing the standardization of chemical preps. and medicaments, P. summarizes the situation as follows: Instead of the terms commonly applied to express the degree of purity of chemicals (crude, tech. pure, purified, chem. pure, absolutely pure, for analysis, for analysis with guarantee certificate), the nature and quantity of the contaminating substances should be indicated in connection with a purity rubric. The principle that it is unscientific and uneconomical to use a chem. prep. of greater purity than necessary for the purpose indicated applies with equal force to medicaments. Accordingly, the practice of most pharmacopoeias in prescribing the highest attainable tech. purity for medicaments in general is not justified. In this connection the use of the product alone should be determinative. It is desirable that pharmacopoeial requirements should, aside from a detn. of the purity, lay greater stress on the chem. compn., form, condition and other properties of preps., by means of standardization, and thus indicate the quality (chem. compn., form, condition, content in active constituents, purity, changes on keeping, and other properties) suited to the purpose in hand. Standardization should include everything calcd. to attain the max. therapeutic effect and utilization of the medicament. Insofar as chem. preps. are involved, the standardization should be carried out by chemists and medical experts in cooperation with representatives of the chem. industry. Any analytical procedure for detg. the purity of a medicament should permit detection of impurities only when the latter are present in max. amt. indicated by the standard for such medicament. For economical reasons only such procedures should be considered which require small amts. of material and reagents. The use of so-called micro-methods is advised. W. O. E.

Application of cryoscopy in pharmacy and food chemistry. P. W. DANCKWORTT. *Z. angew. Chem.* **36**, 358-60 (1923).—The possibility of removing a definite ingredient from a drug or from a solvent applied thereto, and thereby of estg. it from the difference in 2 freezing-point depressions, is discussed, notably in reference to products contg. volatile and fixed oils, alkaloids, etc. Extg. 5 g. of powdered material with 30 g. C₂H₅Br₂ over a period of 24 hrs. before and after elimination of the oil yielded the following values for anis, cardamom, fennel, mace Banda, mace Bombay, cloves: Δ_1 (= before distn.) 0.920, 1.230, 0.820, 2.385, 0.860, 2.115; Δ_2 (= after distn.) 0.525, 0.014, 0.407, 0.656, 0.593, 0.230; $\Delta_1 - \Delta_2 = D$ 0.395, 1.216, 0.413, 1.429, 0.267, 1.885; specific depression

0.778, 0.660, 0.783, 0.774, 0.774, 0.676; % volatile oil 3.0, 11.1, 3.2, 11.1, 2.1, 16.7. Analytical findings also are given for narcotine, thebaine, quinine, yohimbine, papaverine, strychnine nitrate, quinine-HCl and papaverine-HCl, the observations being made on camphor solns. Among the foods examd. cryoscopically were milk and cocoa, with favorable results. The method is apparently susceptible of more general application than heretofore assumed.

W. O. E.

Standardization of insulin. I. Toxicity of insulin for white rats as influenced by temperature of room in which animals are kept. C. VORGLIN AND E. R. DUNN. *U. S. Public Health Repts.* 38, 1747-9(1923).—In a study of the relative toxicity of insulin preps. for white rats as a means of standardization of insulin, it was observed that the toxicity was greater for rats kept at 28-30° than for those kept at 15-7°. The characteristic symptoms of insulin poisoning in the rat also made their appearance more rapidly at the higher temp. Although the explanation for this effect of temp. is not clear, this factor should be carefully controlled in further work. H. B. LEWIS

Orange-flower water and its adulterations. BONIS. *Ann. fals.* 16, 260-8(1923).—Orange-flower water can be distinguished from petitgrain water ("eau de brousts") by the presence of Me anthranilate (absent in the latter) and the ester no. (about 0.3 g. per l. as linalyl acetate for the former and 0 for the latter). There is no known reaction specific of petitgrain water. The combination of Legal's reaction and Duparc and Monnier's modification of the same gives characteristic results with pure orange-flower water. To 10 cc. of the sample in a test-tube add successively: 0.5 cc. of freshly prepd. 10% Na nitroprusside soln. and shake, 2.5 cc. of 5% NaOH and shake, and after 15 secs. add rapidly 0.5 cc. of AcOH, mix rapidly and add immediately 2 cc. of 10% ZnSO₄ soln. After addn. of the AcOH a fugitive emerald-green color is given by genuine orange-flower water, by Me anthranilate and by synthetic oil of neroli. After addn. of the ZnSO₄ genuine orange-flower water immediately gives a violet-red lake, Me anthranilate solns. and synthetic neroli give a green or dead-leaf-colored lake which is slow to form. Petitgrain water gives no coloration after addn. of the AcOH and a dirty yellow ppt. after addn. of the ZnSO₄. For detecting petitgrain water in orange-flower water, B. suggests using the detn. of Me anthranilate as follows: to 10 cc. of sample add 1 drop of H₂SO₄, cool to 0°, add 2-3 drops of 5% NaNO₂ and then a few drops of Na β-naphtholate (β-naphthol 0.5 g., 36° Bé NaOH 5 cc., water 150 cc., Na₂CO₃ 15 g.). The ppt. is not sufficiently pure to be weighed directly and its purification is being investigated.

A. PAPINEAU-COUTURE

Use of some little-known synthetic perfumes. C. R. FLORIANE. *Parfum. moderne* 15, 207-8(1922); *Chimie et industrie* 10, 116(1923).—F. advises the use of aromatic ketones to modify terpenic perfumes, e. g., octyl methyl ketone, hexyl methyl ketone, ethyl amyl ketone. For more flowery and fruity odors, butyrene and benzylone. Propionyl ethylbenzene can be used as a base for clover in conjunction with oil of coriander and oil of cumin. Phenylacetic esters have been used for a long time; p-cresyl phenylacetate is the base for narcissus. It would appear that iso-Pr alc. is the most suitable base for aromatic acids to ensure optimum development of their aromatic qualities. Phenylethyl alc. also lends itself to interesting esterifications, the butyrate being a suitable base for rose perfumes, and the propionate for moss rose. A. P.-C.

The uses of oil of tarragon. C. R. FLORIANE. *Parfum. moderne* 15, 229-30(1922); *Chimie et industrie* 10, 117(1923).—Oil of tarragon is obtained by distn. of *Artemisia dracunculoides*, d 0.900-0.960, [α]_D²⁰ to 0°, n_D²⁰ 1.5028-1.5138, contains principally methylchavicol or estragol, phellandrene, and ocimene. Use in the form of a tincture (50 g. of oil to 1,000 g. of alc.) is advised.

A. P.-C.

Orange concentrate. (Terpeneless orange oil.) E. BERTÉ. *Riv. ital. ess. profum.* 4, 112-3(1922); *Chimie et industrie* 10, 116(1923).—A good oil of sweet oranges yields about 1.5% of terpeneless oil, d₄ 0.880-0.898. The properties vary with the origin, time of extn., soil, and concn. of the oil. A series of analyses is given showing d₁₅ 0.8831-0.9000, [α]_D¹⁵ 25° 50' to 42° 20', aldehydes (as citral) 25.34-43.35%, esters (as linalyl acetate) 14.8%, soly. in alc. 75-80%.

A. PAPINEAU-COUTURE

Determination of esters in concentrated lemon oil and in ordinary oil, from the standpoint of its adulteration with citral from lemon-grass. G. ROMEO. *Riv. ital. ess. profum.* 4, 121-2(1922); *Chimie et industrie* 10, 116-7(1923).—There are two kinds of com. concd. lemon oil: "terpeneless" oil, prepd. by distn. under reduced pressure, d₁₅ 0.8935-0.899, [α]_D¹⁵ -5° to -8° 30', n about 1.431, citral (via Romeo) 40-52%, sol. in 1-10 vol. of 80% alc.; "sesquiterpeneless" oil, prepd. by a special treatment with dil. alc., d₁₅ 0.898-0.902, [α]_D¹⁵ +1° to -3° 45', citral about 65%, sol. in 6-15 vols. of 80% alc., and in 1-3 vols. of 70% alc. The chief adulteration consists in the addition of lemon-grass oil or of citral from lemon-grass. Concd. lemon oils contain 18-25% of

esters (linalyl and geranyl acetates) and the ρ' is lowered by addn. of lemon-grass oil. They should be detd. after elimination of aldehydes by NaHSO_3 . Because of the presence of terpenes in lemon-grass oil, it would be advisable to distil the sample and to det. the esters in the fraction corresponding to the terpenless oil. A. P.-C.

The mechanical extraction of oil of lemon. G. AJON. *Riv. ital. ess. profum.* **4**, 136-7(1922); *Chimie et industrie* **10**, 117(1923).—The ordinary process gives a very fine oil, but the yield is only 60%, a large amt. of the oil remaining in the peel. The mechanical process gives a better yield, but the citral content is decreased and the residue on evapn. is increased. A. PAPISSAU-COUTURE

Investigation of machine-pressed lemon oil. P. LIOTTA. *Riv. ital. ess. profum.* **4**, 137-8(1922); *Chimie et industrie* **10**, 117(1923).—L. gives analyses of samples of lemon oil prepd. with the Lo Verde (Palermo) app. showing the const. vary from those of ordinary lemon oil, more particularly in having a lower citral content. A. P.-C.

Russian ethereal (essential) oils. I. G. V. PROTVLEVSKII. *J. Russ. Phys.-Chem. Soc.* **51**, I, 60-71(1920).—The oil of the pine (*Pinus sibirica*) was obtained by steam distn. of the needles, yield 0.44-0.58%. Two samples of oil from different localities gave the following const.: $d_4^{15.5}$ 0.9155 and $d_4^{17.4}$ 0.9224; α_c -2.08 and +3.84; α_d -2.68 and +4.94; α_e -3.40 and +6.54; α_f -3.96 and +8.06; α_f/α_c , coeff. of dispersion, 1.90 and 2.10; acid no 7.48 and 6.31; sapon. no. (as % of esters, calcd. as bornyl acetate) 46.57 and 44.91, resp. It is pointed out that the 1st sample is levorotatory in distinction from the 2nd and from most European pine oils. Rotation data for various distn. fractions from 80° to 220° are given for both samples. The fractions up to 170° are dextro- and those above are levorotatory. The presence of *pinene* in the 155-6° fractions was shown by the isolation of the nitrosochloride (m. p. 104°), and the presence of *camphene* in the 159-64° fractions by the prepn. of isobornol (m. p. 206-7°). The presence of β -*pinene* is suggested but not proved by the anomalous coeff. of dispersion. The sapon. nos. are claimed to indicate the presence of oxy compds. Two samples of Siberian fir-oil obtained from distn. of the needles and young twigs of *Abies sibirica* gave the following const.: $d_4^{16.4}$ 0.9204 and $d_4^{17.4}$ 0.9202; α_c -31.34 and -31.41; α_d -40.13 and -40.32; α_e -52.66 and -52.26; α_f -63.62 and -63.57; α_f/α_c 2.03 and 2.02; acid no. 2.31 and 0.51; sapon. no. 113 and 108, corresponding to a content of bornyl acetate of 38.85% and 37.8%, resp. With the increase of the h. ps. of the various fractions of this oil a lowering of the rotatory power and the coeff. of dispersion was observed. One sample of oil of juniper (*Juniperus communis*), obtained from the needles and young twigs, yield 0.41-0.58%, gave the following const.: $d_4^{15.6}$ 0.9258; α_c -0.94; α_d -1.16; α_e -1.42; α_f -1.70; α_f/α_c 1.809; acid no. 10.71; sapon. no. 55.33. On fractioning the oil at 30-5 mm. it was observed that 43% of it distd. at 65-9°, and that while this 1st fraction is dextrorotatory, the fractions above are levorotatory. Two samples of oil of peppermint, distd. from the dry leaves of *Mentha piperita*, from 2 different localities of European Russia analyzed as follows: $d_4^{15.6}$ 0.9113 and $d_4^{17.4}$ 0.9019; α_c -21.96, -22.08; α_d -27.66, -27.80; α_e -35.14, -35.26; α_f -41.84, -41.92; α_f/α_c 1.91, 1.90; free menthol 43.58, 45.30%; combined menthol (as acetate) 5.99, 5.71%, resp. The rotatory power for the various wave-lengths of the acetylated oil is also given. One sample of crude (red) and one sample of refined (colorless) pine turpentine, both from Northern Russia, analyzed: $d_4^{14.4}$ 0.8978 and $d_4^{13.3}$ 0.8827; α_c +7.20, +5.16; α_d +9.30, +6.66; α_e +12.40, +8.80; α_f +15.24, +10.66; α_f/α_c 2.12, 2.07; acid no. 2.48, 2.15; 1 vol. sol. in 8 and 8.6 vols. of 80% alc., resp. These figures show lower rotation; greater sp. gr. and also different fractional distn. yields were obtained than those given in the literature for Russian turpentine. This is taken to indicate that the locality of its origin and the differences of soil and climate are important factors in shaping the compn. of turpentines. II. G. V. PROTVLEVSKII AND V. S. NIKITINA. *Ibid* 72-80.—Oil of caraway (*Carum carvi*).—2 samples (nos. 1 and 2) of oil distd. from the seeds alone and 1 sample from seeds and pulp mixed (no. 3) were analyzed with the following results:

| No. | α_c | α_d | α_e | α_f | α_f/α_c | d | Soly. in 80% alc. by vol. | Carvone content |
|-----|------------|------------|------------|------------|---------------------|-----------------------|---------------------------|-----------------|
| 1 | +62.64 | +80.00 | +103.52 | +125.62 | 2.01 | $d_4^{15.5} = 0.9038$ | 1 in 0.7 | 47% |
| 2 | +60.60 | +77.46 | +100.30 | +122.12 | 2.02 | $d_4^{16.5} = 0.9145$ | 1 in 0.6 | 56% |
| 3 | +50.84 | +65.34 | +85.12 | +102.46 | 2.02 | $d_4^{17.4} = 0.9451$ | 1 in 0.4 | 79% |

It is notable that the seed and pulp oil has a much higher carvone content than the seed oil. Oil of pennyroyal (*Mentha pulegium* L.).—One sample from the Caucasus analyzed:

$\alpha_6 + 8.48$; $\alpha_4 + 12.00$; $\alpha_5 + 18.40$; $\alpha_7 + 27.12$; $\alpha_7/\alpha_5 3.2$; $d_4^{16.4} = 0.9301$; *pulegone* content 75%. *Oil of the Caucasian spruce (Picea orientalis)*.—An analysis of 1 sample gave the following figures: $\alpha_2 - 28.39$; $\alpha_3 - 36.38$; $\alpha_4 - 47.42$; $\alpha_7 - 58.10$; $\alpha_7/\alpha_5 2.05$; $d_4^{16.5} = 0.9325$; acid no. 2.17; sapon. no. 97.95, corresponding to 26.42% bornyl acetate. 1 vol. sol. in 2.6 vols. 80% alc. It differs from the oil of the common spruce (*Picea vulgaris*) by a greater content of esters and a lower content of low-boiling hydrocarbons, as shown by fractional distn. *Oil of the Caucasian fir (Abies nordmanniana)*.—This fir is restricted to the higher altitudes (4500–6000 ft.). The oil analyzed was distd. from the needles, yield of 0.34%. The figures obtained are: $\alpha_2 - 29.66$; $\alpha_3 - 38.12$; $\alpha_4 - 49.68$; $\alpha_7 - 60.82$; $\alpha_7/\alpha_5 2.05$; $d_4^{17.8} 0.9410$; 1 vol. sol. in 0.7 vols. 80% alc.; acid no. 3.06; sapon. no. 107.03, corresponding to 28.60% content of bornyl acetate. These figures are similar to those obtained for the oil of the Siberian fir (*Abies sibirica*), except that the Caucasian oil has a higher sp. gr. *Caucasian thuja oil*.—The sample analyzed was distd. from the leaves of *Thuja gigantea*. The figures obtained are: $\alpha_2 - 1.68$; $\alpha_3 - 3.14$; $\alpha_4 - 5.90$; $\alpha_7 - 9.22$; $\alpha_7/\alpha_5 5.49$; $d_4^{16.8} = 0.9260$; acid no. 5.96; sapon. no. 32.03; 1 vol. sol. in 0.6 vols. 80% alc. *Caucasian pine oil (Pinus densiflora)*.—The oil was distd. from the dry needles, yield of 0.37%, and from dried cones, yield of 0.22%. Both oils were from the same locality in the Caucasus. The figures obtained are: $\alpha_2 - 29.98$, -23.72 ; $\alpha_3 - 38.34$, -30.28 ; $\alpha_4 - 49.75$, 39.28 ; $\alpha_7 - 60.81$, -47.44 ; $\alpha_7/\alpha_5 2.03$, 2.00 ; $d_4^{16.5} 0.9124$ and $d_4^{16.4} 0.9602$; acid no. 1.50, 7.60; sapon. no. 91.21, 103.04, resp. *Caucasian and Crimean laurel oils (Laurus nobilis)* analyzed as follows: $\alpha_2 - 18.54$, -18.06 ; $\alpha_3 - 23.26$, -22.79 ; $\alpha_4 - 29.34$, -29.02 ; $\alpha_7 - 34.66$, -34.95 ; $\alpha_7/\alpha_5 1.87$, 1.93 ; $d_4^{15.2} 0.9157$ and $d_4^{15.2} 0.9154$, resp.; soly. of the Caucasian oil, 1 vol. in 0.8 vol. 80% alc. III. *Oils of Crimean fragrant plants*, G. V. FIGULEVSKII AND Y. A. PLOTNITSKII. *Ibid* 81–8.—*Hyssop oil*.—The steam distn. of the blue blossoms of *Hyssopus officinalis* yielded on the av. 0.28% oil as compared with av. yields of 0.23% and 0.165% from white and red blossoms, resp. Preliminary drying of the blossoms reduced the time necessary for complete distn. *Sage oil*.—The distn. of sage (*Salvia officinalis*) plants before blossoming yielded 0.32% of oil as compared with 1.3–2.5% yield from plants after blossoming. *Cypress oil*.—The foliage of a young cypress (*Cupressus sempervirens* L.) yielded on distn. 0.265% oil, while the wood of the trunk and of the larger branches yielded 0.106%. *Juniper oil*.—Finely cut young branches of the *Juniperus excelsa* M. B.-I. *Sabina* L. var. *taurica* Pall yielded on steam distn. a greenish oil with a slight lemon odor, the yield for branches collected in July and August being 0.5% or more. During the distn. the H₂O of condensation was observed to be covered with a layer of fine crystals, a study of which is to be published separately. *Turpentine of the Crimean and of the common pines (Pinus taurica and P. sibirica)*. The saps of these two pines, both from the same locality, yielded on steam distn. 16–20% and 12.6–13.3% of turpentine, resp. Thus the yield of the *P. taurica* is equal to that of the French *P. maritima* and of the American *P. palustris*. The turpentines of both *P. taurica* and *P. sibirica* were found to be levorotatory, $\alpha_D - 17.48$ and -32.11 , resp., in disagreement with previous data which give dextrorotatory figures for turpentines. IV. *Hyssop, juniper and cypress oils*. G. V. FIGULEVSKII AND S. S. FRUNTENKOL'TZ. *Ibid* 87–95.—All of the oils studied were of Crimean origin. The following consts. were found:

| Oil | α_2 | α_3 | α_4 | α_7 | α_7/α_5 | d | Acid no. | Ether no. | Ether no. after acetylation | Soly. in 80% alc. |
|----------------|------------|------------|------------|------------|---------------------|-----------------------|----------|-----------|-----------------------------|-------------------|
| Hyssop blue | -18.72 | -21.32 | -27.54 | -33.60 | 2.01 | $d_4^{14.4} = 0.9382$ | 0.21 | 6.11 | 33.17 | 1 in 0.6 vol. |
| white | -17.08 | -21.80 | -30.00 | -34.40 | 2.01 | | 0.28 | 8.24 | 40.70 | — |
| red | -15.36 | -19.48 | -25.04 | -30.20 | 1.97 | $= 0.9426$ | — | 5.41 | — | — |
| Juniper (July) | +23.16 | +29.20 | +37.24 | +44.52 | 1.92 | $d_4^{16.3} = 0.8896$ | 2.67 | 14.32 | 44.55 | 1 in 9 vol. |
| Cypress young | | | | | | | | | | |
| twigs | +10.80 | +13.08 | +15.66 | +17.34 | 1.61 | $d_4^{12.6} = 0.8729$ | 4.08 | 26.11 | 82.21 | — |
| trunk | -1.24 | -1.40 | -1.64 | -1.80 | 1.45 | $d_4^{16.3} = 0.9153$ | 4.60 | 6.31 | — | — |

W. A. PERLZWIG

The preparation of Heydens Collargol. E. V. ALKSHREYSKII. *J. Russ. Phys.-Chem. Soc.* 53, I, 331–4 (1921).—This investigation is one of the many efforts made by the Russian chemists during the war to reproduce Heyden's patented prepn. A's method is: The whites of 50 eggs were sepd., filtered through fine metal sieves, shaken

in a sep. funnel with a mixt. of 3 g. AcOH, sp. gr. 1.040, and 30 g. petroleum ether of sp. gr. 0.68, and 0.25 g. salicylic acid added as a preservative. After 24 hrs. standing the lowest of the 3 layers consisting of solid impurities and pptd. albumin was run off, and the middle layer of clear albumin soln. was then removed. This was neutralized with dil. NH_4OH , distributed in shallow porcelain dishes and evapd. to dryness in an oven at 40° in a current of air. 50 g. of the dry albumin were dissolved in 250 cc. of an aq. soln. of 8 g. NaOH with 20 min. warming on a water bath. The orange-colored soln. was filtered free of undissolved albumin, and the filtrate was used for dissolving the Ag_2O . The latter was prepd. by pptg. 10 g. AgNO_3 with dil. NaOH, the ppt. washed by decantation and finally dissolved in 30 cc. of the above albumin-NaOH soln. previously dild. to 200 cc. After 1 hr. on the boiling water bath the colloid was pptd. by the addn. of several drops of 80% AcOH, the ppt. was washed with H_2O by repeated decantation, and then it was redissolved by the addn. of 200 cc. H_2O and a few drops of NaOH soln. After 24 hrs. standing the clear soln. was decanted from the undissolved sediment and the soln. evapd. to dryness at 40° in an oven with an air-current. 6 g. of amorphous violet-black lustrous lumps were thus obtained. This end product has a faint pleasing odor, and it is easily sol. in H_2O . No coagulation or sedimentation was observed in a concd. aq. soln. which stood in open beakers for 2 mo., nor on centrifugalization at 2100 r. p. m. On heating the dry product in an open crucible a large amt. of white fumes was given off, leaving a residue of spongy metallic Ag. When heated in the absence of O in a retort an oily material with an odor of NH_3 and some inflammable gases were distd. off. The dry prepn. contains 59.5% Ag. This product as well as the original Heyden Collargol is believed to be not colloidal dispersed Ag, but a mixt. of complex Ag salts of NH_2 acids in a dispersed state.

W. A. PERLWEG

Detection of ethylene derivatives in official anesthetic ether. F. RICHARD. *J. pharm. chim.* 27, 448-55(1923).—The method of the French Codex, 1908, is useless, as the reagent itself (a mixt. of solns. of KHCO_3 and HgCl_2) is unstable. In its place, agitate 20 cc. Et_2O in a glass-stoppered flask with 20 cc. of acid mercuric sulfate (Denig's reagent); neither ppt. nor opalescence will form in the aq. liquid within at least 1 hr. when C_2H_4 compds. are absent.

S. WALDHOTT

El Zair. ANON. *J. Am. Med. Assoc.* 81, 768-71(1923).—El Zair is sold by El Zair Inc. of New York. Originally it was an English prepn. sold variously as "Elixir of Life" and "Elixir of Youth" and was supposed to be prepd. from "mystic herbs" gathered in North Africa. It was sold for consumption, lankness, tuberculous joints, barrenness and other abnormal conditions. The prepn. is designed to be diluted with H_2O and applied externally. Analysis showed $\text{MgSO}_4 \cdot 4\text{H}_2\text{O}$, HCl , $\text{H}_2\text{C}_2\text{O}_4$, 28, oil of bergamot and H_2O to make 100%. It is suggested that the same therapeutic results might be obtained by divided doses of a half lb. of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ in a quart of white vinegar.

L. E. WARREN

The chemistry of digitalis. H. C. HAMILTON. *J. Am. Pharm. Assoc.* 12, 494 (1923).—A succinct statement of the problem confronting chemists. An ext. of digitalis can be prepd. by 70% EtOH which is 100 times as toxic as digitalis leaf. This is partially sol. in CHCl_3 . Both fractions (CHCl_3 -sol. and CHCl_3 -insol.) are active; both give the Keller test; neither is sol. in H_2O but the CHCl_3 -insol. part dilutes with H_2O better. It is impossible at present to purify either fraction to an absolutely uniform activity. An EtOH soln. of these fractions is more stable than tinct. of digitalis. An H_2O -sol. prepn. of these principles is much desired by the pharmacist and clinician.

L. E. WARREN

Balsam of white fir. S. S. AYAR. *J. Am. Pharm. Assoc.* 12, 587-8(1923).—The material was collected from *Abies concolor*, growing in California; $d_{20} 0.989$; $[\alpha]_D 5.53^\circ$; completely sol. in CHCl_3 and Et_2O ; incompletely sol. in EtOH and C_6H_6 . Distn. in steam yielded 27.7% of volatile oil. Oil $d_{20} 0.865$; $[\alpha]_D 11.88^\circ$. About 60% distils at $156-64^\circ$. The presence of pinene in this fraction was demonstrated. Resin mostly sol. in C_6H_6 ; completely sol. in Et_2O and CHCl_3 ; sapon. no. 120.9. L. E. WARREN

Examination of American-made chloramine-T, dichloramine-T, halazone and preparations. P. N. LEECH. *J. Am. Pharm. Assoc.* 12, 592-602(1923).—These products are described in New and Non-official Remedies. The examn. was undertaken to det. the stability and purity of the market products. Chloramine-T. Nine specimens, representing 4 manufacturers, were purchased. The loss at 100° ranged from 8.4 to 18.5%, m. p. $159-69^\circ$, and available Cl content 10.9 to 12.7%. The tablets and paste of chloramine-T and chlorazene surgical cream were of satisfactory quality. One specimen of aromatic chlorazene powder contained but 75% of the amt. claimed, others were but 8% below the declared quantity. Chlorazene surgical powder varied from

30% above the claimed strength to 92%° below. Dichloramine-T. Eight specimens were tested. The m. p. varied from 68 to 83°, available Cl from 25.52 to 29.42%. The market tablets were of good quality. Halazone. The powder contained from 22.92 to 24.08% of available Cl. The N. N. R. standards are 24 to 26.2%. Halazone tablets assayed from 12.5 to 25% below the claimed amt. of available Cl. Specimens of chloramine-T showed but little deterioration after 5 yrs. storage. Halazone undergoes but little change on storage, and dichloramine-T deteriorates somewhat. Chlorazene surgical powder does not keep well, whereas aromatic chlorazene powder is stable.

L. E. WARREN

Study of dental cements. A. LASSIEUR. *Recherches et inventions* 4, 708-18 (1923).—A description of the prepn. of Zn oxyphosphate cement with a brief review of the results obtained by Poetschke (*C. A.* 9, 3289; 10, 1226; 17, 1693). A. P.-C.

Alkaloids. C. H. BÖHRINGER SOHN AND H. STENZL. *Brit.* 192,298, Feb. 21, 1922. Papaverine nitrite is prepd. by the action of salts of nitrous acid on sol. salts of papaverine; the product is freed from papaverine by means of solvents such as benzene, toluene, tetrahydronaphthalene, or alc. The reaction may also be effected in the presence of one of the above-mentioned solvents. Examples of each method are given. The product exhibits the tissue-dilating properties of its components in an enhanced degree.

Lecithin from raw vegetable materials. H. BOLLMANN. U. S. 1,464,557, Aug. 14. Raw materials such as vegetable seeds are extd. with a mixt. of alc. and C₆H₆, benzene or other volatile liquid hydrocarbon material, most of the solvent mixt. is evapd. from the ext., remaining oil is sepd. from its deposit and H₂O vapor is passed into the oil to set free the lecithin. The latter is sepd. and freed from any adhering oil by treatment with H₂O vapor.

Talcum coated with zinc stearate. R. C. FARRELL and C. E. COOGAN. U. S. 1,463,881, Aug. 7. A prepn. for relief of "prickly heat" and similar affections is formed by coating particles of talc with paraffin and Zn stearate.

Disinfectants. J. A. VIELLE. *Brit.* 192,500, Nov. 4, 1921. Tar acids, tar oils and the like for use as disinfectants are prepd. in the form of colloidal dispersions by intensive mechanical disintegration at high speed in presence of H₂O, preferably by means of the colloid mill described in 155,836 (*C. A.* 15, 1788). Small quantities of soap and of free fatty acid may be added to assist in dispersion. An example relates to the treatment of high-boiling cresylic acid.

18—ACIDS, ALKALIES, SALTS AND SUNDRIES

FRED C. ZEISBERG

Viscosities of sulfuric acid-water mixtures. BRADFORD STONE. *Ind. Eng. Chem.* 15, 977(1923).—Attention is called to a correction by Dunstan (*C. A.* 9, 405) to values obtained by Dunstan and Wilson (*C. A.* 1, 956) which brings them into better agreement with results obtained by Rhodes and Barbour (*C. A.* 17, 2937). E. J. C.

The preparation of sulfuric acid and hydrochloric acid from sulfur dioxide and chlorine. BERNHARD NEUMANN AND FRANZ WILCZEWSKI. *Z. angew. Chem.* 36, 377-81(1923).—The reaction SO₂ + Cl₂ + 2H₂O = H₂SO₄ + 2HCl was studied, the undil. gases being used, and it was found to go to practical completion very rapidly, the more rapidly the higher the temp. The resulting H₂SO₄ soln. has a strength of 66-88% and always contains dissolved SO₂, even when an excess of Cl₂ is used. The expts. were carried out both by bubbling the dry gases into H₂O and HCl solns. at temps. from 15° to 90° and with the gases satd. with H₂O at 16.5°, 60° and 90°. The former method gave the better results, the HCl either originally in the soln. or dissolved therein in the early stages of the reaction being driven out as the soln. becomes richer in H₂SO₄. It can be absorbed from the exit gases. The reaction SO₂ + Cl₂ + H₂O = SO₂ + 2HCl, claimed possible by Masson in Fr. pat. 324859, does not take place. F. C. Z.

The recovery of hydrochloric acid used in the process of decalcification of bones. E. V. ALEKSEEVSKII. *J. Russ. Phys.-Chem. Soc.* 53, I, 335-42(1921).—After the bones have been treated with HCl the supernatant soln. is decanted and is treated with (un-slaked) CaO to an alk. reaction. The sedimented Ca₃(PO₄)₂ and the excess of Ca(OH)₂ is filtered off on a press. The alk. filtrate is treated with a sufficient amt. of concd. H₂SO₄ to ppt. all of the Ca in soln. as CaSO₄·2H₂O. The gypsum is filtered off, and the filtrate consisting of fairly pure dil. HCl is made up by the addn. of a calcd. amt. of concd. HCl to the concn. requisite for its reemployment in the decalcification process. A con-

siderable amt. of exptl. data is given on the possibility of almost complete regeneration of HCl from aq. solns. of CaCl_2 by the use of H_2SO_4 and upon the removal of PO_4^{---} with lime.

The catalytic oxidation of ammonia by air in contact with pure palladium. E. DECARRIERE. *Compt. rend.* 177, 186-8 (1923); cf. *C. A.* 16, 2011; 17, 2347.—The surface of palladium used as catalyst for ammonia oxidation becomes roughened like that of platinum, but with decrease in efficiency of oxidation. The optimum temp. is about the same as when platinum is the catalyst, and is unaffected by the condition of the catalyst; the optimum concn. of ammonia is higher. B. H. CARROLL

Preparation of ammonium sulfate in gasworks. A. GREDEL. *Het Gas* 43, 272-6, 309-23 (1923); cf. *C. A.* 17, 1308.—The working methods, especially those of the French gas industry, are reviewed extensively. The av. output is 7.8 kg. $(\text{NH}_4)_2\text{SO}_4$ per 1000 kg. for French or German coal or 11 kg. for English coal. Notwithstanding the production of synthetic NH_3 , the production of NH_3 from gas should be increased considerably. (Cf. *C. A.* 16, 3382.) R. BRÜTNER

Anhydrous aluminium chloride. O. C. RALSTON. *Bur. of Mines, Tech. Paper* 321, 38 pp. (1923).—Information and comment on 11 processes for AlCl_3 manuf. Cheap anhyd. AlCl_3 is essential to the petroleum-refining industry. Properties, uses, cost of raw materials, and means of purification, storage and shipping are given. Patents are reviewed. W. H. BOYNTON

Bismuth, selenium, and tellurium in 1922. V. C. HEIKES. U. S. Geol. Survey, *Mineral Resources of U. S.*, Pt. 1, 15-25 (preprint No. 3, publ. July 16, 1923).

Lead and zinc pigments and salts in 1922. C. E. SIEDENTHAL AND A. STOLL. U. S. Geol. Survey, *Mineral Resources of U. S.*, 1922, Pt. 1, 77-85 (preprint No. 7, publ. July 25, 1923).

Fixation by hydrolysis? K. G. FALK AND R. H. MCKEE. *Chem. Met. Eng.* 29, 224-5 (1923).—The question is asked whether by choice of a suitable catalyst the reaction $\text{N}_2 + 2\text{H}_2\text{O} = \text{NH}_4\text{NO}_3$ cannot be made to go. F. C. Z.

Dry distillation of bones. I, II, III. E. V. ALEKSEVSKII. *J. Russ. Phys.-Chem. Soc.* 53, I, 306-22 (1921).—The best yield of the desired end-products of the destructive distn. of bones was obtained by conducting it in horizontal rather than vertical iron retorts heated to a dull cherry-red. A typical yield under such conditions is: bone-charcoal 68-70%; bone-oil 5.3-6.8%; ammoniacal liquor 17.2-18.4%; volatile fuel gases 5.4-8%. The av. NH_3 content of the liquor is 0.5%. The oil is of $d_{40} = 0.980$. The charcoal contains 9.9% C. It has a high decolorizing power (50% for indigo-carmine). Its adsorptive capacity for salts in soln. is considerable, and it is even greater for gases. These properties render the charcoal suitable for use as a catalyst in the manuf. of phosgene, sulfonyl chloride, and of HCl from the elements or from Cl_2 and H_2O vapor. The exptl. synthesis of $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_3$ effected by passing Cl_2 and $\text{C}_6\text{H}_5\text{CH}_3$ through a tube charged with the bone charcoal at room temp., and also of H_2O from H_2 and O_2 in a similar manner demonstrate the remarkable catalytic properties of the charcoal. It is further shown that the charcoal can successfully replace the CuCl in the Deacon contact process of the prepn. of Cl_2 . W. A. PERLZWEIG

Phosphoric acids; ferro-phosphorus. H. G. C. FAIRWEATHER. *Brit.* 191,642, Feb. 1, 1922. H_3PO_4 , $\text{H}_4\text{P}_2\text{O}_7$ and HPO_3 are obtained by treating phosphatic material, coke, silica and iron in an elec. furnace, oxidizing the liberated P in the furnace by admitting a regulated quantity of air, cooling the gases, and sepd. the acids by an elec. precipitator or other means. When the gases are cooled to 70-120° H_3PO_4 of 70-80% strength is obtained, at 120-210° H_3PO_4 of 80-97%, at 210-315° $\text{H}_4\text{P}_2\text{O}_7$, and at 315-400° HPO_3 . In each case, the H_2O vapor is present in the gases cooled, being introduced in the oxidation air and as moisture in the charge, but additional H_2O may be introduced into the gases. A suitable app. is specified. Cf. *C. A.* 17, 3075.

Catalyst for sulfuric acid manufacture. H. WOLF and F. LLAMA. *Can.* 233,740, Aug. 21, 1923. Vanadium is distributed on a very finely divided carrier and used as catalyst in the manuf. of SO_3 by the contact process. KOH may be used to protect the catalyst from deterioration.

Recovery of potash and alumina from silicates. C. M. BROWN. *Can.* 233,594, Aug. 14, 1923. Finely ground silicates are subjected to the action of HF and SO_2 in a rotary kiln in the presence of air and water vapor and the resulting K_2SO_4 and $\text{Al}_2(\text{SO}_4)_3$ are recovered by leaching.

Barium hydroxide. J. MICHAEL & Co. *Brit.* 192,415, Jan. 29, 1923. BaS is dissolved in hot H_2O and cooled to obtain hydrated crystals. The crystals are sepd.

and heated to 20-100°, dissolved in hot H₂O, and the soln. is cooled to obtain crystals of Ba(OH)₂, while Ba(SH)₂ remains in soln.

Alkali cyanides. F. C. DYCHE-TRAGUE, A. WILSON-HUGHES and F. J. COMMIN. Brit. 192,791, Nov. 11, 1921. Alkali cyanides are made by granulating a mixt. such as equal wts. of Na₂CO₃, C, and Fe₂O₃ (or a mixt. of Fe₂O₃ with 1/10 of its wt. of NiO) by the help of an emulsion of a S-free oil which may be emulsified by means of Na resinates, and heating the granules in a retort, preferably a vertical tube, in a circuit of N at 900-1050°. From time to time H is generated in contact with the granular charge by shutting off the N and introducing superheated steam a little above the cyaniding zone.

Sodium nitrate. GUGGENHEIM BROS. Brit. 192,032, July 24, 1922. Crushed caliche together with fines is leached at atm. or tepid temps., not higher than about 60°, so as to bring the available nitrate into complete soln. The enriched liquors mixed or not with sulfate and with protective agents, to avoid contamination of nitrate with sulfate crystals, are passed through heat interchangers, the temp. range being, *e. g.*, 25° to 6°, and then agitated and further cooled, *e. g.*, to 0°, in refrigerators to remove a portion of the nitrate content by crystn. Mother liquor returns to the leaching tanks through the heat interchangers, and through the NH₃ condenser in cases where cooling is effected by NH₃ vaporization. Impurities consisting mainly of NaCl and Na₂SO₄ remain in soln. at the temp. of the heat interchangers from which nitrate crystals substantially free from sulfate are obtained. Sulfate crystallized in the refrigerators may be removed in known manner or crystn. may be avoided by means of protective agents and regulation of temp. Cf. C. A. 17, 1695.

Boron nitride. S. PRACOCK. U. S. 1,464,292, Aug. 7. B₂O₃ is heated in N to a temp. of about 300° at which it will react with Na. Na is then added to the hot oxide to form B₂N₃. Na₂O is subsequently distd. from the B₂N₃ at about 1100°.

Dehydrating gypsum. F. B. STUART and C. A. RIVERS. U. S. 1,463,913, Aug. 7. Rock gypsum is subjected to steam pressure at 150 lbs. per sq. in. for 4 hrs., after which the steam is cut off, pressure allowed to fall by condensation and the remaining steam blown off.

Chlorine and sulfates from chlorides. F. BERGIUS. Can. 233,741, Aug. 21, 1923. A chloride is treated with H₂SO₄ and available O at a temp. which is always just below the m. p. of the salt mass.

Purifying sulfur chlorides. J. V. MEIGS. U. S. 1,464,137, Aug. 7. Crude S chlorides are treated with a material such as CaCO₃ or pumice capable of removing organic impurities and metallic substances and the crude S chlorides may also be agitated with fuller's earth or other material to effect decolorization.

Oxygen. WOODALL, DUCKHAM, & JONES (1920) LTD., AND J. S. MORGAN. Brit. 192,944, March 1, 1922. O is sepd. from air by absorption in a soln. or suspension of hemoglobin which is prevented from putrefaction by being maintained at about 0° or at a temp. just lower than that at which the hemoglobin coagulates, in presence or absence of a protective colloid. According to an example hemoglobin is circulated counter-current to air in an absorption tower maintained at about 0° and then passed through a vessel where it is subjected to reduced pressure. Another example carries out the absorption at 1.5 atm. and 57°. To avoid frothing while the O is being withdrawn, the soln. may be forced into the low-pressure vessel in the form of a fine spray. Putrefaction is prevented by addition of a germicide, such as hypochlorite, HCHO or a mercuric salt.

Preservation of hydrogen peroxide solutions. A. FARAGO. Can. 233,708, Aug. 21, 1923. H₂O₂ is satd. with O and is brought under high pressure into hermetically closed vessels by means of O.

Production of nitrogen and mixtures of nitrogen and hydrogen. L. CASALE. Can. 233,604, Aug. 14, 1923. A current of air is led into a chamber through an orifice which is surrounded by an orifice through which a current of H is led into the chamber. The air is burned at the point of introduction into the envelope of H formed, water vapor is condensed and the N or H-N product is conserved.

Manufacture of oxides of nitrogen. C. BOSCH, A. MITTASH and C. BRCK. Can. 233,729 Aug. 21, 1923. A mixt. of NH₃ and an O-contg. gas at about 700° is passed over a catalyst contg. an oxide of a metal of the Fe group and an oxide of a rare earth metal, the catalyst consisting of sep. pieces.

Pure retort carbon. I. SZARVASY. Can. 233,715, Aug. 21, 1923. CH₄ is decomposed in an externally heated chamber, which is composed at least at the parts highly heated of pure retort C, the resulting C is deposited on the C walls and both C and walls are crushed together.

Producing and oxidizing phosphorus. B. G. KLUGR. U. S. 1,463,950, Aug. 7. Phosphatic material such as natural phosphate is elec. smelted together with siliceous flux and C or other reducing material to produce P and CO; these are treated with a restricted amt. of air to oxidize the P without appreciable oxidation of the CO.

Phenol-aldehyde condensation products. J. G. BYROM and R. ATTWATER. Brit. 192,941, March 1, 1922. Phenol or cresol is condensed with HCHO with $\text{Na}_2\text{S}_2\text{O}_8$, or other neutral salt of thiosulfuric acid, as catalyst, thus effecting an economy in HCHO, light-colored products being obtained. In an example S-free cresylic acid is condensed in presence of $\text{Na}_2\text{S}_2\text{O}_8$ with HCHO which is added in 4 equal quantities at specified intervals. The product is sepd. from the aq. layer and may be dild. with solvents for use as a varnish or may be incorporated with fillers and hardened for use, for example, as electrical insulation. Cf. 28,009, 1907.

Hydrating lime. N. V. S. KNIBBS and DENNY CHEMICAL ENGINEERING CO., LTD. Brit. 192,278, Jan. 30, 1922. In the hydration of lime and similar reactions between a solid and a liquid the variation in temps. of the reaction mass is utilized to vary the rate at which one of the reacting materials, usually the liquid, is supplied. A suitable construction is specified.

Lime-hydrating apparatus. H. MISCAMPBELL. U. S. 1,464,722, Aug. 14. Lime and H_2O are supplied in regulated amts. periodically to a mixing app. and from this app. the material is passed into an elongated rotating drum for further agitation and uniform hydration.

Sulfur-burning furnace. I. HECHEMBLRIKNER and T. C. OLIVER. U. S. 1,464,527, Aug. 14. Molten S, atomized with air or steam, is burned with a primary air supply and the resulting sulfurous gas is mixed with a secondary air supply to give a product of the desired characteristics.

Plastic mass. H. PLAUSON. Can. 233,180, July 31, 1923. The mass contains a filler and a resin condensed from an aldehyde and ketone in the presence of an alk. condensing agent.

Cleaning contact material. T. I. BRIGGS. Can. 233,308, Aug. 7, 1923. Foreign substances are removed from contact substances mounted on fibrous material without disarranging the material, by introducing water into the receptacle holding the contact substance at a place below the latter until it is submerged, shutting off the water, introducing water into the receptacle above the substance and discharging the water from the receptacle below the contact substance.

Treating hoofs. C. D. NIVEN. Brit. 192,658, May 19, 1922. Hoofs and articles, such as combs, made therefrom, are steeped in a soln. of HCHO or in the waste liquor obtained in the curing of casein with HClHO.

Friction power transmission. L. E. GRANTON. Brit. 192,729, Sept. 12, 1921. A compn. for preventing or minimizing the slipping of frictional power transmitting members contains silicates of Na or K or mixts. thereof or water glass, as binding material, and filling materials such as powdered SiO_2 , asbestos, pumice stone, or kaolin, with or without substances such as Zn powder for preventing rusting and substances such as $\text{K}_2\text{Cr}_2\text{O}_7$, tannic acid, or casein for reducing brittleness and assisting the drying. Starch may be added to increase the adhesiveness. The ingredients are intimately mixed and colloided as far as possible. The compn. is applied directly to the pulley, etc., or may be applied to leather, balata, cotton, etc., pulley coverings.

Preventing condensation on glass. L. LEWIS. Brit. 192,340, Sept. 7, 1922. A soln. of soft soap in methylated spirit is specified.

19—GLASS, CLAY PRODUCTS, REFRACTORIES AND ENAMELED METALS

G. E. BARTON, C. H. KERR

Use of the autoclave test as a method of testing glassware. W. H. WITHEY. *J. Soc. Glass Tech.* 6, 289-91 (1922).—While of very great use for glasses designed for contact with steam or water under pressure, the autoclave test in general is much too severe for ordinary ware. Two glasses alike in their resistance to attack at a low temp. may differ at a higher temp. and the order of their difference may be inverted at a still higher temp.; under the appropriate conditions suited to their characteristics both may be equally good. Tests described on a Zn borosilicate and a lime borosilicate glass showed that under prolonged treatment the former flaked, continually exposing a fresh surface to the corroding agent, while the latter acquired a "bloom" through which the corroding agent had to penetrate to reach the glass surface. J. S. C. I.

Analysis of bubbles in glass. RESEARCH STAFF OF GEN. ELEC. CO., LONDON, (J. W. RYDE AND R. HUDDART). *Proc. Phys. Soc. London* 35, 197-8(1923).—In order to distinguish bubbles generated by chem. action in glass from those introduced by mech. processes, spectroscopic tests are made for the presence of N. To liberate the gas from the bubbles, a specimen of the glass is placed in one limb of a quartz U-tube and Hg in the other, and the glass is heated and then disintegrated by sudden cooling, the tube being plunged into cold H₂O at the same time that the Hg is thrown on to the glass.

C. C. VAN VOORHIS

Some aspects of the autoclave test for durability of glass. W. L. BAILLIE. *J. Soc. Glass Tech.* 6, 279-88(1922); cf. *C. A.* 16, 2204.—Durability depends not only on the corroding agent employed, but on the method of manuf. and the purpose for which the ware is designed. The use of accelerated tests possibly introduces disturbing factors. The use of glass powder is not recommended, as the surface exposed cannot be estd., there being no simple relation between sieve grading and grain vol. Further, cementation between grains probably occurs when the decompn. becomes extensive and this prevents both free access of the corroding agent to the whole surface and the removal of all the alkali in the final washing stage. The autoclave test executed on finished pieces of suitable size, or on test blocks cut from finished ware and having the cut surfaces weathered for some time before use, is flexible and capable of producing results in close agreement. Steam is recommended in preference to water as a corroding agent, and times and pressures are conveniently varied to suit the type of glass under test. Thus a series of glasses may be sharply differentiated at 4 atm. pressure, while at 10 atm. all may be equally bad, in which case 4 atm. will be a suitable pressure for the test. Rise of temp. does not accelerate the action of steam on all glasses to the same extent, which may be due to the fact that decompn. is the result of two reactions differently accelerated by temp. rise. The effect of increasing the pressure is not so easily accounted for. It is suggested that high pressures may promote reactions which do not occur at pressures nearer atm. *E. g.*, Turner (*C. A.* 16, 4026) found that with glass rich in alkali the alky. at 5 atm. was greater than that at 25 atm.

J. S. C. I.

The lime, cement, ceramic and glass laboratory of the Conservatoire National des Arts et Métiers, Paris. ANON. *Recherches et inventions* 4, 690-6(1923).—Description of the equipment.

A. PAPINEAU-COUTURE

The burning of porcelain with fuel oil. A. GRANGER. *Chimie et industrie Special No.*, 330-2(May, 1923).—Operations at the Royal Copenhagen Porcelain Works and at Sèvres have shown that fuel oil can be successfully used and is much more flexible than coal or wood.

A. PAPINEAU-COUTURE

Tile making in Czechoslovakia. RUDOLF BARTA. *Rev. Mat. Constr. Trava. Pub.* 161, 21B-22B(1923).—There are 12 factories with a capacity of 90,000 tons, of which 72,000 tons are exported to European countries. One of the better clays is that of Brestany, analyzing SiO₂ 64.43, Al₂O₃ 10.70, TiO₂ 0.51, Fe₂O₃ 1.51, CaO 2.70, MgO 0.34, KNaO 2.81, H₂O 7.90%. When washed it passes through 180-mesh, with only 0.02% residue. It softens at cone 7, and fuses at cone 10. The natural color is yellow or red, other colors being obtained by the addn. of coloring oxides. The clay left over winter in a damp state, then dried at 100°, is put through a mixer; it then passes through a 15-mesh screen. The moisture content is 5-7%. The tile are burned in saggars, in large round kilns, and fired at cones 6-10, in an oxidizing atm. The tile are subjected to tests: (1) texture of break, (2) petrographic study for size of grain and distribution of material, often showing 5% SiO₂ and 95% glass, (3) sp. gr., (4) porosity, (5) hardness, (6) resistance to compression, when dry, wet and after 25 repeated heatings and coolings, (7) resistance to wear.

LOUIS NAVIAS

Glass manufacture. CORNING GLASS WORKS. *Brit.* 192,919, Feb. 7, 1922. The colors due to metallic salts in glasses, particularly the borate glasses colored by CoO or NiO, are modified by adding a substance or substances contg. one or more of the halogens. When KCl is added to the batch of glass contg. a very high proportion of boric oxide and colored with CoO, the resultant glass has a green color instead of red. The color change is less noticeable when the proportion of boric oxide in the glass is low or when other halide salts are used instead of the chloride.

Glass manufacture. V. HORDK. *Brit.* 112,713, Feb. 5, 1923. A resistance glass is made from a batch contg. 60-70% of SiO₂, 15-30% of boric oxide, 1-2% of K₂CO₃, 3-6% of Na₂CO₃, 2-6% of kaolin, up to 4% of mica, and 1-3% of an oxide of the silicon group, *e. g.*, Zr or Ti. The glass is stated to have a low coefficient of expansion, a high fusing point, and great resistance to chem. action.

Enameling. K. WARGA. *Brit.* 191,771, Aug. 16, 1921. Multicolor decorations,

designs, lettering, etc., are printed on surfaces of Al or Al alloy and enameled. Films comprising mixts. of mineral colors or pigments and vitreous flux with a liquid or viscous vehicle are printed successively on the metal surface, the melting points of the mixts. being so arranged that the mixt. adjacent the metal surface has the lowest m. p. and the m. ps. of the successive films rise progressively. The metal surface is oxidized prior to printing and the films are fixed by firing in a kiln in which a temp. corresponding to the highest m. p. is maintained.

Flutriation of clay and kaolin. B. SCHWERIN. *Can.* 233,737, Aug. 21, 1923. The clay is put into suspension and brought to the sol. condition by the addition of a suitable electrolyte, it is then allowed to settle.

20—CEMENT AND OTHER BUILDING MATERIALS

J. C. WITT

Developments in the cement industry. R. FURNESS. *Chemistry and Industry* 42, 728-31(1923).—The cement industry in the principal countries of the world has interested itself keenly in the scientific study of problems related to the manuf. and use of cement, though a relative lack of attention has been paid to problems of a fundamental nature. Increases in kiln economy have resulted from the use of insulating materials and improved refractories, and the installation of waste heat boilers. Other developments include the recovery of potash; reduction of the amt. of water in slurry; control of draft, stack gases and temp. in the kiln; investigations of the influence of the modulus of fineness or apparent specific gravity of cement, in addition to that of fine grinding, *per se*, upon the general properties of portland cement; the investigation of integral waterproofing agents; inquiries into the optimum amounts of water, aggregate, etc., and into the best size of aggregate for concrete making; expts. on the influence of salts, etc., on the setting, hardening, disintegration, etc., of concrete; and many other problems in the making, use, storage, handling, and transport of cement. The high-alumina cement manuf. in France presents a possibility of revolutionary changes in the cement industry.

J. C. WITT

Disintegration of cement in sea water. W. G. ATWOOD AND A. A. JOHNSON. *Proc. Am. Soc. Civil Eng.* 49, 1038-64(1923).—A review and bibliography. J. C. W.

The effect of alkali on portland cement. K. STEIK. Wyoming Agr. Expt. Sta., *Circ.* 16, 4 pp.(1922).—(Of the salts which may be present in alkali $MgCl_2$ has the greatest disintegrating effect upon concrete followed by Na_2SO_4 and $MgSO_4$. $NaCl$ increases the harmful effects of sulfates and Na_2CO_3 decreases it. $NaCl$ when present alone has almost no effect. Mortars contg. small quantities of cement disintegrate in less time. The age of cement before it comes in contact with solns. of alkali does not seem to have a great effect on rate of disintegration.)

J. J. SKINNER

Insecticides, fungicides, preservatives [for wood] (Brit. pat. 191,793) 15.

Pitch cement. G. A. HENDERSON and R. G. ERWIN. U. S. 1,464,480, Aug. 7. A cement adapted for use in paving construction is formed of pitch which has been vulcanized with 1-5% of Cl, H_2S and SO_2 in the presence of protective colloids and a vulcanization accelerator, *e. g.*, clay, Cl, H_2S , $CuSO_4$, Na_2SO_4 and $NaCl$.

Bituminous concrete. G. A. HENDERSON. U. S. 1,464,481, Aug. 7. A concrete wearing surface for roads of a thickness of 1.5-3 in. is formed of mineral aggregate the interstices between which are filled with a bituminous material contg. bitumen 43-52% mixed with 48-57% of mineral dust of colloidal sizes comprising Na_2SO_4 , $CuSO_4$ and with S derivs. such as H_2S and SO_2 . This wearing surface layer is united monolithically with a bituminous macadam base.

Bituminous concrete. G. A. HENDERSON. U. S. 1,464,482, Aug. 7. A bituminous conglomerate adapted for paving is formed of vegetable fibers impregnated with a relatively hard bituminous material of a ductility exceeding 60 cm. at a temperature of 25° together with colloiddally suspended kieselguhr in particles all passing a 200-mesh sieve and acting as the continuous phase in colloidal dispersion of the vegetable fibers.

Waterproof fibrous sheets. L. KIRSCHBRAUN. U. S. 1,464,717, Aug. 14. Waterproof sheets, *e. g.*, sheets of fiber, clay and asphalt, are coated with a similar mixt. contg. a smaller proportion of fiber. *Cf. C. A.* 16, 2766.

Building sheets, slabs, etc. W. A. OSBORNE. Brit. 192,205, Nov. 9, 1921. Tan bark, sawdust, wood flour, or a mixt. of these materials is mixed with calcined magnesite,

MgCl₂ and glue, and the compn. is molded into sheets, blocks, moldings, or like building units.

Bituminous road binder. C. N. FORREST. U. S. 1,464,928, Aug. 14. An emulsion miscible with H₂O, which, when used as a road binder, dries out and thereby becomes immiscible with H₂O, is prepd. from heavy asphaltic oil or other similar material and sulfonated derivs. from mineral oil distillates.

Bituminous paving mixtures. F. S. BESSON. U. S. 1,464,488, Aug. 7. A graph or chart is given for detg. the proper amt. of bitumen to be used for making a satisfactory paving mixt. on the basis of preliminary detns. of the void percentage and sp. gr. of the aggregate used. If the voidage is 41% and the sp. gr. of the aggregate is 2.7, a bitumen content of 8.2% is used.

Preserving wood. R. A. MARR, JR. U. S. 1,464,044, Aug. 7. A mixt. for impregnating wood is formed of a solidifiable petroleum base such as paraffin or asphalt, a petroleum oil of the same base, creosote, rosin and diatomaceous earth.

21—FUELS, GAS, TAR AND COKE

A. C. FIELDNER

Products yielded by carbonization of coal at low temperature. J. D. DAVIS. *Fuels & Furnaces* 1, 247-9(1923).—Any coal that will produce high-temp. coke will in general produce low-temp. coke. Those most suitable include the bituminous coals contg. from 4.5 to 5.8% of H and 87 to 89% C. Representative analyses of coke made from Freeport coal are given.

D. F. BROWN

Utilization of very low-grade fuels by mixed firing. PILLARD. *Technique moderne* 15, 475(1923).—Properly conducted mixed firing (use of two different kinds of fuel) can improve the combustion of the two fuels, allow of good combustion of very low-grade fuels with high water content or low volatile, increase the flexibility of boiler operation and decrease the amt. of smoke. Using a combination of fuel oil and very low-grade fuel (which could not be used alone) consisting of a mixt. of unburnt C from automatic stokers and of slag, with a calorific value of 700-1000 cal. the evapn. from 0° at 100° per kg. of oil was 2.81, higher than with fuel oil alone, and the C was completely burned. A furnace with mechanical stoker equipped for mixed firing showed 9-10% CO₂ in the flue gas when only coal was being burned and 15-16% as soon as the oil burners were lit. In a hand-fired furnace burning lignite the evapn. was 4500 kg. and the flue gas temp. 220°; with lignite and fuel oil the evapn. rose to 7800 kg. and the flue gas temp. to only 240°.

A. PAPINEAU-COUTURE

Report on the work of the Scientific Committee of the (French) National Fuel. GEORGES BAUME. *Chimie et industrie* Special No., 706-13(May, 1923). A. P.-C.

The rational use of various liquid fuels in internal-combustion engines. F. SCHWERS. *Chimie et industrie* Special No., 682-701(May, 1923).—A discussion of the mechanism of the combustion, max. thermal efficiency, and max. power production.

A. PAPINEAU-COUTURE

Fuels having an alcohol base. W. R. ORMANDY AND E. C. CRAVEN. *Chimie et industrie* Special No., 635-7(May, 1923).—A discussion of the miscibility of 95% alc. and gasoline, and of the effect of Et₂O and of higher alcohols as stabilizers. (Cf. *C. A.* 16, 1694, 3380, 3423.)

A. PAPINEAU-COUTURE

Motor fuels, especially alcohol. FREDERICK L. NATHAN. *Chimie et industrie* Special No., 627-34(May, 1923).—A discussion of the possibility of finding suitable substitutes in sufficiently large quantities for petroleum products, especially gasoline.

A. PAPINEAU-COUTURE

Alcohol as fuel. E. HADDON. *Rev. agr. Maurice* 1, No. 9, 129-30(1923).

F. W. Z.

Results obtained in Spain with various alcohol, naphthalene, and turpentine fuels. M. CHAMBIGE. *Chimie et industrie* Special No., 702-5(May, 1923).—A fuel consisting of alc. 35, benzene 35, gasoline 20, Et₂O 10% showed a consumption about 26% higher than gasoline when used in gasoline engines without any modification. A mixt. of alc. 30, naphthalene 5, mineral oil 2, Et₂O 10 showed a consumption about 33% higher than gasoline, and the motors had to be completely overhauled and cleaned after running 1500-2000 km. A mixture of alc. 63, spirits of turpentine 25, Et₂O 10, castor oil 2% showed a consumption 63% higher than gasoline with a fairly abundant deposit of easily removed C. The motor had to be cleaned after 20,000 km. or more. There is considerable corrosion when no castor oil is used, and but little when it is used. Results

show the possibility of using a mixt. of alc., benzene, gasoline, Et_2O and spirits of turpentine (with 2% of castor oil), and the unsuitability of an alc. soln. of naphthalene.

A. PAPINEAU-COUTURE

The fuel question from the standpoint of common carriers in the City of London. OWEN W. J. WATSON. *Chimie et industrie Special No.*, 675-9(May, 1923).—A brief outline of the most important results obtained by the L. G. O. Co., in exptg. with various mixts.: benzene-alc.; benzene-alc.- Et_2O ; alc.- Et_2O , showing the drawbacks of each. It cannot be satisfactorily abstracted.

A. PAPINEAU-COUTURE

Hygroscopicity of absolute alcohol. Manufacture and use for the preparation of liquid fuels. P. LORLETTE. *Chimie et industrie Special No.*, 718-21(May, 1923).—Treatment of a gasoline-alc. mixt. with a dehydrating agent (K_2CO_3 , CaO , CuSO_4 , etc.) to stabilize the mixt. and prevent sepn. into two layers raises the strength of the alc. only to 99%, and the mixt. remains homogeneous only to -10° . Abs. alc. (99.8-99.9%) can be obtained directly without a rectifying column by passing alc. vapors over CaO (cf. LORLETTE, C. A. 17, 2470). A mixt. of 99.9% alc. (15%) and heavy gasoline (85%) was exposed at 15° to a moist atm. (80% humidity), the ratio of exposed surface to vol. being 0.2. After 12 days it still remained clear when cooled to -22° ; and after 43 days it clouded at -8° . Abs. alc. (99.8%) under the same conditions fell to 99.2% in 3 days and to 95.65% in 21 days, and 96.4% alc. fell to 92.55%.

A. P.-C.

The mutual solubility of alcohol and gasoline in presence of a third solvent. A. ROTHEN AND D. BOUTIER. *Chimie et industrie Special No.*, 733-4(May, 1923); cf. BAUME, *et al.*, C. A. 14, 3776.—The mutual soly. of alc. and gasoline depends on the strength of the alc., on the nature of the gasoline, which in turn depends on the crude oil and on the method of distn., and on the nature and amt. of the third solvent used. A table and curves are given showing the clouding point when varying amts. of benzene, Et_2O , Me_2CO , iso-Pr alc., iso-Bu alc., normal Bu alc., Am alc., cyclohexanol, butyl cresol, castor oil, and terpineol, resp., are added to various alc.-gasoline mixts. Bu alc., Am alc., cyclohexanol and butyl cresol are the best solvents studied; iso-Pr alc. and terpineol are fair; iso-Bu alc. and Me_2CO are poor; and benzene, Et_2O and castor oil are practically worthless. Tetralin and wood turpentine ("benzine de bois") are less efficient than Me_2CO .

A. PAPINEAU-COUTURE

Navy has anti-knock fuel for airplanes. ANON. *Nat. Petroleum News* 15, No. 31, 80(1923).—A mixt. of 70 parts aviation gasoline, 28% abs. alc. and 2% benzene is being used exclusively at the naval air stations at Anacostia, Hampton Roads and Pensacola. This mixt. works satisfactorily at high compressions without detonation. D. F. B.

Gasoline substitutes for use in miners' lamps. ENRIQUE HAUSER. *Chimie et industrie Special No.*, 338(May, 1923).—A benzene-alc. mixt. should contain not over 22.50% benzene to prevent smoking; and this mixt. has 0.77 the illuminating power of gasoline in a Marsaut lamp. A mixt. of 96% alc. 60-65, benzene 25-20, gasoline 15% has 0.98 the illuminating power of gasoline. A mixt. of 96% alc. 62.0, benzene 16.0, rect. spirits of turpentine (fraction distg. below 155°) 7.50, and fusel oil 14.50% has 1.32 times the illuminating power of gasoline, but it has a disagreeable odor and slightly soils the wick. This could be reduced by decreasing the amt. of turpentine and of fusel oil.

A. PAPINEAU-COUTURE

Modern processes for the extraction of benzene from coal gas. CH. BERTHÉLOT. *Chimie et industrie Special No.*, 571-7(May, 1923).—A critical review of the oil, cresol, charcoal and refrigeration processes, showing particularly the merits of the refrigeration process.

A. PAPINEAU-COUTURE

A new fuel for explosion motors from tar distillation. L. ROMAN. *Chimie et industrie Special No.*, 583-8(May, 1923).—"Cosmoiline" consists of benzene 70, naphthalene 30, cresol 1.5, naphthylamine 0.25, nitronaphthalene 0.25 parts. Results of tests are described showing it to work as satisfactorily as gasoline and benzene in motors without any change in adjustment of any of the parts.

A. PAPINEAU-COUTURE

Benzene from the standpoint of a (French) national liquid fuel. J. ERHARD. *Chimie et industrie Special No.*, 579-82(May, 1923).—A discussion showing that benzene cannot become an economically important factor as a substitute for petroleum and its products.

A. PAPINEAU-COUTURE

The treatment of tars and of benzenes for the production of liquid fuels. P. PEIFFERT. *Chimie et industrie Special No.*, 542-58(May, 1923).—A review of the processes used and of the properties and applications of the fuels obtained.

A. P.-C.

The liquid fuel problem in its relation to the low-temperature carbonization of coal. EDMOND CONNERADE. *Chimie et industrie Special No.*, 531-41(May, 1923).—A review covering processes used for low-temp. carbonization.

A. PAPINEAU-COUTURE

The lignite of Southern Bohemia and its gasification. J. KAVAN. *Chimie et*

industrie Special No., 465(May, 1923).—A typical analysis gave H₂O 5, ash 12.3%, calorific value 2040 cal. With lignite contg. 66% H₂O a lean gas was obtained with calorific value of 950 cal. per m.³ at 0° and 760 mm. The condensed water from the producer contained 0.2–0.22% MeOH, which could easily be raised to 0.5% (allowing of economical recovery) by using only the most ligneous portions of the lignite. A. P.-C.

Brief description of the French lignite deposits. BRUNSCHWIG. *Chimie et industrie Special No.*, 445–53(May, 1923).—See C. A. 17, 199. A. P.-C.

The lignite of Hérault and of Aude (France). DE PRITZBUER. *Chimie et industrie Special No.*, 454–8(May, 1923).—The deposits and some of the mines are briefly described. Low-temp. carbonization tests, which are described in detail, show the possibility of obtaining an exceptionally high amt. of tar which yields valuable oils.

A. PAPINEAU-COUTURE
The lignites of Hérault. CARTERET and DEVAUX. *Chimie et industrie Special No.*, 459–60(May, 1923).—Lab. expts. in an elec. still gave 180–225 kg. of tar per ton. Com. tests in an old Pieters furnace gave about 170 kg. per ton. By low-temp. carbonization about 58.5% of the S remains in the coke, 6% in the tar and 35.5% in the NH₃ waters.

A. PAPINEAU-COUTURE
Lignite in Serbia. DE PRITZBUER. *Chimie et industrie Special No.*, 461–3(May, 1923).—The deposits are briefly described, and analyses of lignites and of the gas and tar obtained on low-temp. carbonization are given.

A. PAPINEAU-COUTURE
The tertiary boghead coal of Bohemia. FERDINAND SCHULZ. *Chimie et industrie Special No.*, 464(May, 1923).—The calorific value on the dry and ash-free basis goes as high as 9000 cal., and the volatile 70–79.5% of the combustible material. This boghead is really a "wax coal" which has been transformed by very high pressure and other geological influences. Part of its bitumen content is insol. in C₆H₆. Cf. C. A. 17, 2039.

A. PAPINEAU-COUTURE
Methods of investigation of lignite. EMILIO DAMOUR and M. LAFARGUE. *Chimie et industrie Special No.*, 466–8(May, 1923).—The theoretical max. yield of oil from lignite by low-temp. carbonization to *t*^o is the greatest amt. which can be obtained by progressive distn. stopping at *t*^o. Two conditions are essential in detg. it: heating must be sufficiently gradual so that the products distg. at a given temp. be completely removed while the mass is still at that temp., and the heat must be properly distributed so that the products of distn. are at no time subjected to a temp. higher than that at which they were evolved. These conditions are fulfilled by a cylindrical furnace with peripheral elec. heating and central chimney for drawing off the gases. Two types of Copaux furnaces (capacity 15 kg.) built along these lines are described. Comparative lab. tests with a Copaux furnace and with a horizontal retort heated with coal gave: max. temp. 600, 625°; dehydrated tar per ton 53, 39 kg.; gas per ton 140 m.³, 210 m.³, resp.

A. PAPINEAU-COUTURE
Modern ovens for the low-temperature carbonization of lignites. C. BERTHELOT. *Chimie et industrie Special No.*, 470–6(May, 1923).—A description of the Fischer, Weisenberger, Nielsen, Carbocoal, and Salerni retorts, with a discussion of their relative merits from the standpoint of obtaining max. yields of oil.

A. PAPINEAU-COUTURE
Condensation, distillation and recovery of by-products from lignites. C. MARILLER. *Chimie et industrie Special No.*, 492–5(May, 1923).—Brief review. A. P.-C.

Discussion of the utilization of peat bogs. F. SCHWERS. *Chimie et industrie Special No.*, 496–505(May 1923).—Critical review of the various processes of drying peat.

A. PAPINEAU-COUTURE
Peat and its commercial utilization as a fuel. EMILIO DAMOUR. *Chimie et industrie Special No.*, 507(May, 1923).—Peat can be economically used in a Riché gas producer provided it contains not over 40–50% H₂O and its cost is not more than one-third that of coal. Its use in admixt. with garbage in incinerators has been found advantageous.

A. PAPINEAU-COUTURE
The industrial utilization of peat. LUCIEN TONNELLE. *Chimie et industrie Special No.*, 477–91(May, 1923).—A description of the working of peat bogs in France since 1917 showing the errors committed and how to avoid them, and describing some successful results obtained. Cf. C. A. 17, 198.

A. PAPINEAU-COUTURE
Peat as a fuel. HELLEMANS. *Chimie et industrie Special No.*, 503–20(May, 1923).—A general discussion of the conditions under which peat can be used successfully and of the proper furnace design.

A. PAPINEAU-COUTURE
Use of peat in gas producers. MARCEL LAFFARGUE. *Chimie et industrie Special No.*, 521–6(May, 1923).—A critical review.

A. PAPINEAU-COUTURE
Application of vegetable oils as fuels for heating and power purposes. CHARLES. *Chimie et industrie Special No.*, 769–74(May, 1923).

A. PAPINEAU-COUTURE

Tests with vegetable oils in Diesel and semi-Diesel engines. P. DELAHOUSSE. *Chimie et industrie Special No.*, 704-6 (May, 1923).—Brief outline of results obtained by various French engine constructing firms in successful tests with palm, peanut, and cottonseed oil and Karité butter. A. PAPINEAU-COUTURE

Mechanical traction in the (French) colonies. R. E. MATHOT. *Chimie et industrie Special No.*, 759-63 (May, 1923).—Tests carried out in 1920-1921 have shown that palm, cottonseed and castor oils can be used in two and four cycle engines. Changes which should be made in the construction of the engines to give optimum results with this class of fuels are discussed. A. PAPINEAU-COUTURE

Mechanical stokers and the chemical industries. W. H. WOOD. *Ind. Eng. Chem.* 15, 918-20 (1923).—A discussion of reasons for the prevalence of hand firing in the chem. industries. Characteristics of standard types of stokers are described, with their applicability to various solid fuels and to chem. plant conditions. A. E. MARSHALL

The testing station of the Comité Central des Houillères de France. ANON. *Recherches et inventions* 4, 615-20 (1923).—Description of the Monthaçon station erected to continue the work started at the Livvin station destroyed towards the end of the war. A. PAPINEAU-COUTURE

Reversing valves for regenerative furnaces. G. H. ISLEY. *Fuels & Furnaces* 1, 255-7 (1923).—The qualities of an ideal reversing valve for regenerative furnaces are enumerated and a description is given of the Isley valve designed to meet these requirements. D. F. BROWN

Water-gas production in horizontal retorts. J. RUF. *Helv. Gas* 43, 286-92 (1923).—A lecture. R. BEUTNER

Lean gas producer. Blowing superheated steam. Enriching the gas and recovering the sensible heat. LAFFARGUE. *Technique moderne* 15, 475 (1923).—Installations of one producer cannot be forced. By heating the primary air to 300° and adding 200 g. of H₂O per kg. of C the calorific value of the gas is raised 100 cal. per m.³. If the air is heated by means of the sensible heat of the gas the economy is 6%. With a battery of producers the no. of units can be reduced and the rate increased. If the temp. is kept sufficiently high and 450 g. of H₂O per kg. of C is injected the calorific value is raised 250 cal. per m.³, and the radiation loss is reduced by an amt. equiv. to 7.5% of the C gasified. If the air is heated by means of the sensible heat of the gas there is a further economy of 7.5%. A. PAPINEAU-COUTURE

Heat balance of carbonization process. J. K. MUNSTER. *Blast Furnace & Steel Plant* 11, 389-92 (1923).—Retabulation and discussion of the data collected by Chamberlin and McGovern (*C. A.* 17, 1320) on a battery of 106 Koppers coke ovens. Results show carbonization to be exothermic to extent of 210 B. t. u./lb. A separate balance of combustion for heating the oven shows 3 main sources of loss of heat: in the hot coke, 41.17%; in hot raw gas, 24.47%; and in stack gases, 26.67%. J. J. MORGAN

The production of low-temperature tar and its transformation into motor fuel. FRANZ FISCHER. *Chem. Weekblad* 20, 390-7 (1923).—A lecture. R. BEUTNER

The nature of the hydrocarbons present in low-temperature tar light oil. FRANZ SCHUTZ. *Brennstoff-Chem.* 4, 84 (1923).—In low-temp. tar light oil there have been identified paraffins, olefins, diolefins, cyclic diolefins, aromatic hydrocarbons, hydroaromatic hydrocarbons. C. T. WHITE

Dry distillation of rice and oats chaff. J. MARCUSSEON and M. PICARD. *Chem. Ztg.* 47, 585 (1923).—500 g. of rice hulls (chaff) heated for 1-1.5 hrs. in a 3-l. glass retort began distg. at 120°, attained its max. between 200 and 300°, and was completed at 400°. The yield was 6% oil, 33% aq. distillate, 41% carbonaceous residue, and 20% gases. The oil was brownish black, sol. in twice its vol. of abs. alc., and upon fractionation gave 11% b. 120-170°, 16% b. 170-300°, 23% b. 230-270°, 28% b. above 270°, 17% coke and 5% loss. The fraction above 270° is very fluid, contains only 0.7% of paraffins, and is made up chiefly of anhydrides of oxyacids, phenols and fatty acids. It resembles wood tar. The aq. distillate contains 4% AcOH. The gases consist of 30-37% CO₂, 0.3-2.7% heavy hydrocarbons, 2.4-4.4% O₂, 30.2-37.5% CO, 2.1-6.6% H₂, 11.8-18.6% CH₄ and 4.7-11.6% N₂, with an av. heating value of 2700 heat equivs. The carbonaceous residue was friable, contained 38% of ash (chiefly SiO₂), and was without decolorizing power when tried with sugar sirups and mineral oils. Oats chaff gave results similar to those recorded above. W. C. EBAUGH

Quantitative determination of sulfur forms in coke. A. R. POWELL. *Ind. Eng. Chem.* 15, 951-3 (1923); cf. *C. A.* 17, 869.—Coke contains S in 4 forms, as FeS, S₂, free S adsorbed on the surface of the coke, and S held in solid soln. in the carbon. The total S in coke may be detd. by any one of the well known methods. Then two 2-g. samples, 35 mesh in size or smaller, are accurately weighed out and one is placed in

a 200-cc. Erlenmeyer flask. This sample is used to det. the FeS sulfur. This is done according to the standard procedure, by adding HCl and adsorbing the H₂S evolved in CdCl₂ soln. The contents of the Erlenmeyer flask are filtered and any SO₄ is pptd. as BaSO₄. The second sample is placed in a porcelain boat which is inserted in a silica tube. The SO₄ sulfur, and free S are reduced with H at red heat. After cooling the contents of the boat are placed in an Erlenmeyer flask and the same procedure is followed as for the detn. of FeS. The S thus found represents the sum of the FeS, SO₄, and free S. The free S can be calcd. by subtracting from this figure the amts. of FeS and SO₄ sulfur which have been previously detd. The FeS, SO₄, and free S content of the coke being known, by subtracting the sum of these in terms of % of S from the total S in the coke, the % of solid soln. S will be known. C. T. WHITE

Use of hot, dry, moist and oxygenated blasts in gas producers, cupolas and blast furnaces (SEIGLE) 9.

Fuel. H. DUPUY and L. LAIS. Brit. 192,418, Jan. 29, 1923. Pulverulent fuel, e. g., poor coal, anthracite, etc., is molded with a binder of resins, etc., into briquets which are provided with a perforation preferably along their major axis. The briquets are distd. so as to form a smokeless fuel, the distn. products being collected.

Carbonizing coal. P. DVORKOVITZ. Brit. 192,816, Nov. 17, 1921. Coal, or other carbonaceous material is carbonized at a temp. between 280° and 500° by the passage therethrough of heated gas in such a manner that the heating is greater at the top of the retort than at the bottom end from which the distillates are removed and a yield of hydrocarbons of the paraffin series is obtained. A suitable construction is specified.

Carbonizing coal, etc. W. C. WHITE. Brit. 192,040, Oct. 26, 1922. In the low-temp. carbonization of coal, lignite, peat, shale, wood and similar carbonaceous materials, hot gas after passage through a rotary retort contg. the material is cleaned and preheated before being again circulated through the retort, a part of the gas and distillates being removed from time to time. A suitable construction is specified.

Fuel briquets. J. W. BURROUGH. Brit. 192,892, Jan. 16, 1922. Equal parts of cement and dry ground clay are mixed and then incorporated with 8 or 9 parts of sawdust, shavings, etc., and worked with H₂O into a plastic mass; this is pressed into dies. Wet clay may be used, the sawdust and cement being stirred into a slurry of clay and water. One part of fine coal or similar combustible may be added to the ingredients, the proportions of cement and clay then being slightly increased. On removal from the dies the briquets are allowed to stand until hard, and may be dried in ovens or by means of a hot air blast; they may be dipped in or sprayed with a crude mineral oil.

Agglomerating combustible substances. SOC. DE RECHERCHES DE PERFECTIONNEMENTS INDUSTRIELS. Brit. 192,369, Dec. 8, 1922. In the sepn. of combustibles from incombustible substances by agglomeration one or more cryst. or colloidal substances in soln., apparent soln. or emulsion, are added to reduce the surface tension of the bath of oil and H₂O. Examples of substances used are soaps, resinates, or saponins; a suitable proportion for Na resinate is 1 in 1000.

Gas manufacture. C. B. TULLY. Brit. 192,880, Dec. 20, 1921. In app. for the complete gasification of coal in which a retort is arranged above a gas producer and is heated externally by the "blow" gases, the retort is made of such a size that it will contain an amt. of coal of about one-half to two-thirds of the daily throughput of the gas producer.

Distillation of solid carbonaceous materials. H. NIELSON and B. LAING. Brit. 192,515, Nov. 10, 1921. In the distn. of carbonaceous materials the heating medium consists of hot combustion gases which, after being utilized for distg. purposes and being thereby enriched with combustible gases, are admixed with air and reignited for the purpose of subjecting further quantities of materials to heat treatment. A suitable construction is specified.

22—PETROLEUM, LUBRICANTS, ASPHALT AND WOOD PRODUCTS

F. M. ROGERS

Direct observation of the hydration of hydrocarbons. PAUL WOOD. *Compt. rend.* 177, 207-8(1923); cf. C. A. 17, 3094.—Satd. oils assume a turbid appearance when exposed to water vapor at ordinary temp. while the unsatd. oils under similar

treatment retain their original transparency. W. connects this with the phenomena observed in the spreading of the oils on water.

J. A. ALMQUIST
Gasoline absorption process. E. KAY. *Oil & Gas J.* 22, No. 12, 52, 78-80(1923).—A general description of the absorption type plant for making casinghead gasoline.

D. F. BROWN

Using vapor-phase process for cracking. L. DE FLORES. *Refiner & Nat. Gasoline Mfr.* 2, No. 8, 7-10(1923).—A simple vapor-phase cracking equipment consists of 8 furnaces each contg. a single vertical coil of 1.5 in. tubing, which is reduced to 1 in. in the cracking zone. Oil passes through these tubes at velocities as high as 16,000 ft. per min. and thence into an expansion tank. The oil is pumped at 200 lbs. pressure and passes through a suitable air chamber and strainer, after which the pressure is reduced by individual needle valves on each unit, so that the pressure at the intake of the tubes is 75-125 lbs. The pump pressure and tube pressure are both registered on the same dial, giving ready means for detg. the condition of the tubes. The expansion chamber is fitted with a lining which can be easily removed for cleaning. The process is designed for handling oils of 36-42° Bé. gravity. Cost of construction of the plant is about \$60,000. Max. daily capacity is about 1000 bbls. of charging stock per day. Cost of operation is 25 c. per bbl. of charge stock and 15 c. additional for refining and treating.

D. F. BROWN

The Greenstreet process of cracking. F. HYNDMAN. *Oil Eng. & Finance* 4, 81-2(1923).—A brief description of the process is given. Gas oil of 29.3° Bé. and distg. through a straight condenser from a flask as follows: 215-250° 4%, 250-300° 20%, 300-360° 44.5%, over 360° 31.5%, when treated by this process distd. as follows: up to 100° 8%, 100-150° 10, 150-200° 8, 200-250° 8, 250-300° 18, over 300° 37, loss about 5%.

D. F. BROWN

Compression and absorption plants. L. F. BAYER. *Oil & Gas J.* 22, No. 11, 54 (1923).—A brief description and comparison of the 2 methods of making casinghead gasoline.

D. F. BROWN

Determination of the tar number of mineral oils. E. CASIMIR. *Petroleum Z.* 19, 763-5(1923).—Detn. of the tar no. of mineral oil by the Holde method, the Marcusson-Schwarz petroleum ether extn. method and by the Kramer $C_{12}H_{22}$ extn. method are compared.

D. F. BROWN

The oil fields of Mexico. ANON. *Petroleum Times* 10, 201-3(1923).—A summary of the present status of the oil industry in Mexico.

D. F. BROWN

The Dutch East Indies oil region. ANON. *Petroleum Times* 10, 176(1923).—A general description of the region. Three kinds of oil are produced: (1) a heavy oil found at depths of from 30 to 290 meters, of sp. gr. 0.96 to 0.89 (this oil yields no fractions boiling below 150°), (2) a lighter oil, sp. gr. 0.88 to 0.85 coming from depths of 200 to 400 meters, (3) a paraffin oil, sp. gr. 0.86 to 0.84 coming from greater depths.

D. F. BROWN

Occurrence of petroleum in Georgia. ANON. *Petroleum Z.* 19, 723-4(1923).—An historical account of the oil fields in this country. The oil occurs in both the eastern and western sections of the country. It is usually a greenish brown and ranges in gravity from 0.83 to 0.93.

D. F. BROWN

The Trumble topping process. R. R. MATTHEWS. *Oil News* 11, No. 16, 15-6 (1923).—A brief, non-technical description of the Trumble pipe still, which is claimed to be the first system of its kind installed in this country.

D. F. BROWN

Practical considerations on fuel oil and its applications. M. DE BREY. *Chimie et industrie Special No.*, 239-49(May, 1923).—A review covering properties, handling, and uses for heating, with a discussion of its advantages.

A. PAPINEAU-COUTURE

Liquid fuels and their commercial uses. FRANÇOIS GAUDIN. *Chimie et industrie Special No.*, 250-84(May, 1923).—A review concerned only with petroleum products.

A. PAPINEAU-COUTURE

Fuels for Diesel engines. R. PONCHON. *Chimie et industrie Special No.*, 285-7 (May, 1923).—A discussion of the properties required for Diesel engine fuels.

A. PAPINEAU-COUTURE

A new process of bituminous shale distillation. E. DE LOISY AND E. GRAUCK. *Chimie et industrie Special No.*, 434-8(May, 1923).—The process consists essentially in treating the shale in a gas producer, using air mixed with a portion of the fixed gases produced after sepg. the oil, and condensing the products of distn. With a somewhat makeshift app. over 1000 tons were treated from Aug., 1921, to March, 1922, which shows it was commercially practicable. The yield was about 70 l. per m.² (900 kg.), nearly the same as that obtained in Scotch retorts with the same shale, and 10-12 kg. of $(NH_4)_2SO_4$ per ton of shale. The function of the gas injected with the air is two-fold: its combustion takes the place of the primary combustion of the fixed C of the shale (which caused superficial slagging of the shale); it then reacts with the fixed C and gasifies it by means of an

endothermic reaction which prevents slagging. The oil had a d. of 0.930, slightly higher, than that of the oil obtained in Scotch or French retorts, which is probably due partly to incomplete condensation of the lighter distn. products and partly to absence of cracking of the distd. oil. The phenol content (about 6%) is about the same as that of oils obtained in retorts, but it contains 16-17% of unsatd. hydrocarbons as against 8-9% in oils obtained by the usual processes. The amt. of outside fuel required is calcd. at about 0.5-0.6% of the shale treated; and about 350 m.², having a calorific value of 1,100 cal., will be available per ton of shale.

A. PAPINEAU-COUTURE

Modern furnaces for the distillation of bituminous shales. CH. BERTHELOT. *Chimie et industrie Special No.*, 439-42 (May, 1923).—A description of the Scotch retort, Fischer rotary furnace, and Salerno horizontal furnace.

A. PAPINEAU-COUTURE

Scotch bituminous shales. E. M. BAILEY. *Chimie et industrie Special No.*, 423-8 (May, 1923).—A description of the distn. process and purification of the oil. Cf. C. A. 17, 1326.

A. PAPINEAU-COUTURE

Note on the Estonian shale deposits. MARCEL E. DE JARNY. *Chimie et industrie Special No.*, 429-32 (May, 1923).—Description of the deposits and of the expl. distg. plant of the Estonian govt.

A. PAPINEAU-COUTURE

The bituminous shale and boghead coal (torbanite) industry. PHILIP DUMAS. *Chimie et industrie Special No.*, 387-93 (May, 1923).—A discussion of the importance of bituminous shales and of boghead coal as a source of oil and of NH₃.

A. P.-C.

Brief description of the French bituminous shales. BRUNSCHWIG. *Chimie et industrie Special No.*, 394-7 (May, 1923).

A. PAPINEAU-COUTURE

Bituminous shales. A. CAMBRAY. *Chimie et industrie Special No.*, 398-410 (May 1923).—A description of bituminous shales, their properties and methods of working them.

A. PAPINEAU-COUTURE

The bituminous deposits of the Largue Valley (France). PH. RICHEMOND. *Chimie et industrie Special No.*, 411-9 (May, 1923).—Description of the geological formation and of the work done on the deposits.

A. PAPINEAU-COUTURE

Recovery of oils from bituminous shales, peat, coal, etc. HERMANN PLAUSON. *Petroleum Times* 10, 87-9 (1923).—The process consists in mechanically driving off the substance to be recovered by means of superheated steam or inert gas moving through the mass of coal, etc., at a rate of about 300-600 meters per sec. Thus the org. constituents of bituminous shale can be recovered in nearly theoretical quant. yield if steam superheated to about 350° and under 8 atms. of pressure is passed through layers of shale 30-50 cm. thick. The temp. on the other side of the layer is not over 105-120°. Oils are thus obtained without decompn. and yield up to 50% of low b. p. hydrocarbons (80-200°). The same yield at a lower temp. is possible if 1-3% of a solvent like benzene, gasoline, etc., be used.

D. F. BROWN

An outline of lubricant making. G. M. LARSON. *Oil News* 11, No. 16, 39-40 (1923).—A brief general description of the manuf. of lubricating oils from paraffin and asphalt base crude oils, and discussion of their relative merits.

D. F. BROWN

Lubrication of heavy oil engines. H. MOORE. *Oil Eng. Finance* 2, 525 (1922).—M. divides heavy engines into 3 classes in considering lubrication: Diesel engines in which the fuel is injected by high pressure air; cold starting engines in which it is injected by mech. means; and hot bulb engines in which it is injected by mech. means and ignited by a hot bulb or plate. High viscosity oils are not necessary on Diesel engines. Oil for lubrication of enclosed high speed engines must have a high flash point (above 420° F.) to avoid possibility of crankcase explosions. Lubrication of the compressor is more difficult than that of the engine. The liquid from the compressors has been found to contain, in addn. to water, formic and acetic acids. Formation of these acids is minimized by the use of oils of low I no. These oils, however, do not possess the same property of film maintenance as the asphaltic oils. Three-stage compressors do not generate so much acid as the 2-stage compressors. Engines not employing compressed air are more easily lubricated. Mineral oils compounded with 5 to 7% of rape, coconut or lard oil are suitable for cylinder lubrication of these engines. Asphaltic base mineral oils are also suitable. Hot bulb engines require higher viscosity oils for lubrication than do the first two classes of engines.

D. F. BROWN

The lubrication of internal-combustion engines burning heavy oils. HAROLD MOORE. *Chimie et industrie Special No.*, 325-9 (May 1923).—A discussion of the types of lubricants best suited for the various types of this class of engines. Cf. preceding abstr.

A. PAPINEAU-COUTURE

What oil for steam engines? F. A. HOFF. *Oil News* 11, No. 16, 28-9 (1923).—Factors controlling the choice of lubricating oils for steam engines are: type of engine; boiler steam pressure; length of the steamline; kind of steam, i. e., wet, dry, superheated,

etc.; method of feeding oil to the cylinder; and covering on the steam line. When the steam is very wet the following compd. is recommended, 90% of 27 gr., 540 flash, 600 fire, 40 cold test, 140 viscosity oil (mineral), and 10% acidless tallow oil. For reasonably dry steam this ratio is changed to 94% and 6% of the above. For superheated steam use a straight mineral lubricant of 650 to 700 fire test. For slowly moving pumps or any machinery where condensation is high use a compd. of 90% 600 steam-refined stock and 10% acidless tallow oil. In a Corliss engine use 96% of the mineral oil and 4% of the tallow oil in the high-pressure cylinder and 92% and 8% of these stocks, respectively, in the low-pressure cylinder.

"Germ process" lubricants. H. M. WELLS. *Oil News* 11, No. 16, 17-8(1923).—It has been shown that addition of 1% fatty acids to mineral oils increases the lubricating power of the oil 17%. Also correct and adequate grooving in bearings and journals adds 17-22% in efficiency compared with ungrooved bearings. Emulsification troubles with steam engines and turbines have been overcome by the addition of fatty acids to the regular lubricant.

Practical lubrication. W. F. STACK. *Oil News* 11, No. 16, 37(1923).—A general discussion of lubrication problems.

Asphalt and related bitumens in 1922. K. W. COTTRILL. U. S. Geol. Survey, *Mineral Resources of U. S., 1922*, Pt. II, 7-13(preprint No. 3, publ. July 19, 1923).

Russian turpentine. Systematization of quality, nomenclature, and trademarks. B. SMIRNOV. *Chem. Trade J.* 72, 599-600, 635-6, 663-4(1923).—S. seeks to establish the value of different types of Russian turpentine, and to formulate a rational nomenclature that can be used in the trade. A color scale using various strengths of KI-1 solns. has been devised to accord with the tints (yellow to red) which prevail in turpentine and which are due to resins in soln. Various com. turpentine have been classified in accordance with the colors in this scale and also with the methods used in present-day production in Russia. S. also outlines methods used in the fractional distn. of turpentine. The fraction b. 160-70° is the important one, but n_d , $[\alpha]$, and ignition points are not sufficient to characterize the samples. The industrial factors influencing the quality of the turpentine are briefly discussed, and the merits of 3 types of installation used in Russia are outlined.

LOUIS E. WISE

Deposit of bitumen in a lava-cavern in Bombay (WADIA) 8. Action of H_2PO_4 on rosin, wood tar, etc. (MELAMID, ROSENTHAL) 10.

Cracking hydrocarbons. HOOVER CO. Brit. 192,106, Aug. 22, 1921. In converting high-boiling hydrocarbons into lower-boiling oils by heating with $AlCl_3$, the sludge, which forms in the reaction vessel, is withdrawn while liquid and before the catalyst in it is completely spent, and is sprayed into a heated chamber to cause vaporization of $AlCl_3$. The vapors may be washed with hydrocarbon oil to absorb the $AlCl_3$, which is returned to the reaction chamber. The process is carried out in the app. described in 189,200 (C. A. 17, 2498).

Cracking and hydrogenating hydrocarbon oils. F. BERGIUS and S. LÖFFLER. Brit. 192,856, Nov. 30, 1921. In prepg. light hydrocarbons by heating mineral oils or heavy hydrocarbons, which may be mixed with coal, brown coal, lignite, turf, etc., under a pressure of about 100 atm. with or without H, as described in 25,510, 1913 (C. A. 10, 116), 4574, 1914, and 18,232, 1914 (C. A. 10, 386), the materials are heated to about the reaction temp. before being introduced into the reaction chamber. The reaction chamber, which may be made with thin walls, is heated by hot gases, such as CO_2 , circulating in a jacket under a pressure about equal to that used in the reaction chamber. A suitable construction is specified.

Cracking and hydrogenating hydrocarbon oils. F. BERGIUS and S. LÖFFLER. Brit. 192,849, Nov. 30, 1921. In prepg. light hydrocarbons by heating heavy hydrocarbons or mineral oils, which may be mixed with C, under pressure as described in 25,510, 1913 (C. A. 10, 116), or under pressure in presence of H as described in 4574, 1914, and 18,232, 1914 (C. A. 10, 386), the reaction chamber is heated by hot gases such as CO_2 or combustion gases, circulating in a surrounding jacket under a pressure about equal to that used in the reaction chamber. A slight difference of pressure indicated by a water column may be used to indicate if the walls of the reaction chamber sustain damage. The oil or a mixt. of oil and C prepd. as described in 192,850 (cf. above) is fed from a tank through a heater and H from a receiver through a heater. Vapors from the reaction chamber pass by a pipe to condensers and residue is withdrawn through another

pipe. The heating gas from the jacket is circulated through a heater and is returned by a pump.

Recovering unsaturated hydrocarbons from gases and vapors. C. ELLIS. U. S. 1,464,152, Aug. 7. Light volatile oils are obtained by the action of H_2SO_4 (preferably in the form of a film or spray) upon gaseous or vaporous hydrocarbon material contg. unsatd. hydrocarbons, *e. g.*, gases from petroleum oil cracking. The light volatile oils thus obtained as polymerization products are adapted for use in making alcs.

Reaction tower for treating hydrocarbon vapors with scrubbing liquids or other reagents. B. ANDREWS. U. S. 1,464,918, Aug. 14. The app. is especially adapted for scrubbing vapors from cracking stills with liquid hydrocarbons.

Ethylsulfuric acid from olefinic gases. C. ELLIS. U. S. 1,464,153, Aug. 7. Still gases such as result in oil cracking are treated during cooling with H_2SO_4 , the effective strength of which is progressively reduced during reaction to such an extent that H_2SO_4 of about 1.8 sp. gr. is reduced until reactive acid liquor of 1.4 or lower sp. gr. is obtained. Residual gases are treated with H_2SO_4 of higher strength than 1.8 sp. gr. at a temp. above 60° until ethylsulfuric acid of sp. gr. of 1.4 or lower is obtained.

Regenerating anhydrous aluminium chloride. G. R. STEUART. U. S. 1,464,373, Aug. 7. In treating residues contg. $AlCl_3$ and petroleum coke, the C is oxidized to the gaseous state to liberate the occluded $AlCl_3$ and the latter is converted to Al_2O_3 and Cl by the O present and the high temp. The Al_2O_3 and Cl are then further heated in a reducing atm. to effect their recombination to produce $AlCl_3$.

Crumpled aluminium alloy packing. C. C. HALL. U. S. 1,464,604, Aug. 14. A material suitable for packing stuffing boxes is formed of annealed, crinkled and crumpled sheets of Al alloy contg. at least 60% Al. This material is coated with graphite and lubricating oil of high fire test and is folded and compacted together.

Gasoline-purifying apparatus. W. C. CLOVER. U. S. 1,464,071, Aug. 7. Gasoline is treated with NaOH and washed with H_2O after use in "dry-cleaning" clothes.

Oil still. N. H. FREEMAN. U. S. 1,464,246, Aug. 7. A horizontal oil still is divided by a horizontal partition into 2 compartments communicating with each other only through the partition near one end of the still. Oil to be distd. is fed into the upper compartment and after it has traversed the length of both compartments residue is withdrawn from the lower compartment. Vapors are withdrawn from the upper compartment and the temp. of the still is controlled thermostatically.

Separating wax from petroleum oil lubricating stock. C. H. HAPGOOD. U. S. 1,464,707, Aug. 14. Lubricating oils contg. waxes are subjected to two successive refrigerating treatments to throw the waxes out of soln. followed by centrifuging to sep. the oil from the pptd. wax. In the second refrigeration, the stock is cooled by direct expansion of NH_3 and in the first refrigeration heat exchanged between the wax-free oil and the stock is utilized to cool the latter.

Cooling and "quick-aging" hot charcoal. O. F. STAFFORD. U. S. 1,464,732, Aug. 14. Hot charcoal is brought into contact with N and CO_2 or other cool inert gas to cool it considerably and an O-contg. atm. is then gradually substituted for the inert gas and the charcoal is held in contact with the O-contg. gas, *e. g.*, air, at a high-aging temp., preferably about $50-60^\circ$.

23—CELLULOSE AND PAPER

CARLETON E. CURRAN

The present position of cellulose research. E. DÖRR. *Z. angew. Chem.* 36, 399-402(1923).—A review with references. E. J. C.

Cellulose determination by means of phenol. L. KALB AND V. SCHOELLER. *Cellulosechemie* 4, 37-40(1923).—The encrusting materials (lignin, etc.) of plant fibers are readily removed if the finely divided material (passing a sieve having 100 meshes per sq. cm.), purified by successive treatments with H_2O and acetone, is dried and treated with 12.5 parts of dry PhOH and very small amts. of HCl at water bath temp. for several hrs. For spruce wood, 4-g. samples were used with 50 g. PhOH and 25-200 mg. HCl. After several hrs. the mass was washed with H_2O and dil. NaOH, filtered, washed with H_2O , aq. AcOH, and again with water, and weighed. The % cellulose is somewhat lower than that given by the Cross and Bevan method, but is much higher than that obtained with König's method. Consistent results were also obtained for beech wood, sulfite pulp, and cotton. The method cannot be used to det. total polysaccharides in fibers, since the delignification also causes partial hydrolysis of the polysaccharides. This partial hydrolysis can possibly be controlled in such a way that hemi-

celluloses and pentosans may be removed from the cellulose, in which case the method has marked advantages over König's method.

LOUIS E. WISE

Decomposition of wood by means of phenol. EBERHARD LEGGLER. *Cellulosechemie* 4, 61-2(1923).—Summary of the results given in L.'s dissertation (Berlin-Charlottenburg 1921) and in subsequent patents. Wood meal, heated with PhOH and very small amts. of HCl (as little as 0.03% of the wt. of PhOH) or compds. readily converted into HCl, is practically freed from lignin in 15 mins. Under similar conditions, but in the absence of HCl, heating for 7 hrs. leaves the wood practically unaffected. When anhyd. PhOH and HCl were used, the residual pulp had all the chem. properties required of a good com. material. Diln. of the PhOH with H₂O or EtOH lowered the quality of the pulp. Optimum temp. for carrying out the "cook" was 70-80°. The process does not promise to be commercially successful because of L.'s failure to recover large amts. of the phenol used in delignification, which apparently condenses with the lignin to form resins sol. in PhOH.

LOUIS E. WISE

Cellobiose. S. V. HINTIKKA. *Cellulosechemie* 4, 62(1923).—Cellobiose was prepd. from cotton, spruce pulp, soda pulp, and from straw, by Freudenberg's method (C. A. 15, 2721) and converted into the *heptabenzoylate*, micro-needles, m. 202-4°, by treatment with BzCl and NaOH. The benzoylation also yielded 2 other products which were not purified.

LOUIS E. WISE

Hydrocellulose. EMIL HEUSER AND GEORG JAYME. *Ber.* 56B, 1242-3(1923).—Mol. wt. detns. of the dimethylhydrocellulose described in C. A. 17, 875 have now been successfully carried out in freezing H₂O; the results (737-73) agree well with the calcd. value for [C₁₂H₁₈O₆(OMe)₂]_n (760).

C. A. R.

Hydrocellulose. II. Decomposition by means of oxalic acid. EMIL HEUSER AND FRITZ EISENRING. *Cellulosechemie* 4, 13-21, 25-31(1923); cf. C. A. 17, 875. The properties of hydrocellulose (A) from viscose cellulose by Knoevenagel and Binsch's method (C. A. 16, 2779) are not materially changed by protracted treatment with HCl, although the yields of A gradually decrease. The % of H₂O present during the reaction, however, influences not only the yield but the character of the entire reaction. The yield of A drops with increasing amts. of H₂O in the reaction mixts., and the product becomes more and more readily hydrolyzed by subsequent treatment with H₂SO₄. The primary products of HCl hydrolysis of the viscose cellulose appear to be dextrans, whereas the use of fuming HCl gives quant. yields of glucose. The sol. NaOH derivative of A is C₁₂H₁₈O₆·2NaOH. Treatment of viscose with oxalic acid under carefully regulated conditions gives a hydrocellulose identical with A, but the reaction may go much farther if the concn. of oxalic acid and the temp. are increased, with the production of 65% glucose, and the decompn. of oxalic acid into CO, CO₂, H₂, and H₂O. Quant. yields of glucose are not obtained since the latter is converted in part into hydroxymethylfurfural (cf. Kiermeyer, *Chem.-Ztg.* 1895, 1005). Somewhat greater amts. of the same decompn. products are obtained when A is treated with oxalic acid. A much less extensive hydrolysis was noted when ordinary cotton cellulose was heated with 5% oxalic acid. Only 15-16% of glucose was obtained under these conditions, and the residual hydrocellulose was incompletely sol. in NaOH. Dil. mineral acids acting upon cellulose also give rise to small amts. (1-3%) of hydroxymethylfurfural. L. E. WISE

The soluble cellulose esters of the higher fatty acids. H. GAULT and P. EHRMANN. *Compt. rend.* 177, 124-7(1923).—A resumé and collection of the researches on the sol. esters produced by the action of the higher fatty acids on cellulose. R. C. ROBERTS

The cellulose acetates. ANON. *Chem. Trade J.* 73, 155-7(1923).—A review. E. J. C.

Action of bacteria on cellulosic materials. A. H. LYMAN and HERBERT LANGWELL. *J. Soc. Chem. Ind.* 42, 279-87T(1923).—Steaming stable manure contains a bacillus which attacks almost every form of cellulose under either anaerobic or aerobic conditions. Lignocelluloses (wood, jute) and cuto-cellulose (cork) were attacked slowly if at all, unless the cellulose was first freed from combination. The optimum temp. of growth of this bacillus is 60-68°, but for comparison the tests on standard media were carried out at 20-38°, the growth at lower temps. being similar to, though not so rapid as, that at the higher temps. The best results were from bacteria grown on glucose agar plate at 37°. In the expts. an active cellulose culture was plated under pure culture conditions and a single colony used to start another cellulose culture. A single organism appears to be responsible for the anaerobic fermentation of cellulose, and this organism is different in behavior on standard media from any species known to the authors. A list of 8 resistant celluloses, 5 modified celluloses, 7 hemicelluloses, 2 starches and 5 sugars shows the common forms of carbohydrates which have been successfully fermented. In some of the tests from 200 to 600 lbs. of cellulose were used. Bleached

cotton waste, sulfite pulp, and Whatman's No. 40 filter paper fermented from 5 to 15 days left an insol. org. resid. of 7 to 15%. This gelatinous residue was largely bacteria as the microscope revealed but few fibers. A table shows the results of 10 typical fermentations of celluloses and sugars under varying conditions. Among the products AcOH can be made to vary from 20 to 80% of the original cellulose, butyric acid 0 to 30, lactic acid 0 to 60, EtOH 0 to 30, and methane 0 to 8%. Equations are given showing the probable course of fermentation in order to account for the products formed. Over-aeration results in the oxidation of any of the above-named products to CO_2 and H_2O . Practically the heavily lignified cellulose such as wood and xylem of perennial plants must be made into chem. pulp to render the cellulose fermentable. Green plants require only mech. pulping. With dry materials a light boil with very dil. H_2SO_4 makes pulping easier and also hydrolyzes the pentosans to xyloses which are fermentable. A lengthy discussion followed the presentation of this paper. L. W. R.

The paper industry: Problems and recent developments. BJARNE JOHNSEN. *Ind. Eng. Chem.* 15, 891-3(1923). E. J. C.

Testing for rubber latex in paper. ANON. *The Paper Makers Monthly* J. 61, 8, 341(1923).—The paper is treated with CHCl_3 and after standing one hr. the mixt. of paper and CHCl_3 is warmed. The paper is removed and the CHCl_3 evapd. until 2-3 cc. remain. Glacial AcOH is added until a persistent white ppt. appears which coagulates on standing, which indicates the presence of latex in paper. The rosin remains in soln. The ppt. has a characteristic appearance under the microscope. F. G. R.

The quantitative estimation of hemp and wood fibers in paper pulp. W. DICKSON. *Analyst* 48, 372-8(1923).—D. detcs. the proportion of the two kinds of fibers by Spence and Krauss' method (*World's Paper Rev.* Dec. 18, 1917), making no correction for differences in wt. of the different fibers. Ordinary and polarized lights are used to identify the fibers. Magnifications of 100 and 400 diameters are most useful. Photomicrographs by ordinary and polarized light are shown. The procedure is described in detail. A. PAPINEAU-COUTURE

Hypobromite method of determining bleach requirements of pulp. T. M. ANDREWS AND M. W. BRAY. *Ind. Eng. Chem.* 15, 934-7(1923).—Tingle's method was modified to prevent loss of bromine vapor. 0.75 g. of pulp contg. less than 10% moisture is shaken with 30 cc. of a mixt. of nine parts by vol. of HCl (sp. gr. 1.19) and one part H_2SO_4 (sp. gr. 1.84) in a glass stoppered flask. The mixt. after diln. with 300 cc. water is brought to 23°, 10 cc. of 0.1 N Br in alkali is added and the mixt. shaken at intervals for 20 min. The excess Br is estd. by addn. of KI and titrating with standard $\text{Na}_2\text{S}_2\text{O}_3$, and the Br consumed is calcd. as Cl. Three times the Cl requirement gives the bleaching powder figure. This method gives good results with sulfite pulps, but not with soda pulps. F. G. R.

Bleach studies on wood pulps. II. C. G. SCHWALBE AND H. WENZL. *Papierfabr.* 21, 277-9, 281-2(1923); *Paper* 32, No. 10, 9-10, 21; No. 11, 5-6, 28(1923); cf. C. A. 17, 2783.—Acidification of the bleaching bath with CO_2 gives positive results only when the acid is added to the alk. liquor before the addn. of the pulp. The combined acid-alk. process attacks the cellulose and leads to the formation of oxycellulose. Yellowing of bleached pulp occurs when the bleach chemicals have not been completely washed out. Yellowing increases with increase in the alky. of the bleach soln. and decrease in the temp. of reaction. An acidification of 0.1%, or less, with dil. acid has a favorable influence on bleaching. J. L. PARSONS

Determination of gypsum in waste sulfite liquor. A. SANDER. *Chem.-Ztg.* 47, 336-7(1923); *Papierfabr.* 21, 283-4(1923); *Paper* 32, No. 12, 5-6, 17(1923).—The methods offered in the literature for the detn. of CaSO_4 in waste sulfite liquor are not entirely free from errors in that difficulty is experienced with the org. matter present. S. treats a sample of the liquor with concd. HCl in an atm. of H_2 or CO_2 . Following the decompn. of the org. acids and the removal of most of the SO_2 , the mixt. is heated on a water bath to which NaCl has been added. The lignin ppt. is removed by filtration and the sulfates in the filtrate are pptd. with hot BaCl_2 soln. Some org. matter comes down with the BaSO_4 and allowance is made for the subsequent reduction to BaS on ignition by adding H_2SO_4 and heating again. The residues were white. CaSO_4 is more sol. in waste sulfite liquor than in H_2O . J. L. PARSONS

Colloid-chemical studies on the rosin sizing of paper. I, II. W. O. OSTWALD AND R. LORENZ. *Kolloid-Z.* 32, 119-37, 195-209(1923); *Paper* 32, No. 11, 76(1923).—By the acidification of a soln. of Na resinatc γ -pinic acid, m. about 76°, is pptd. By repeated crystn. from dehydrating solvents, such as abs. EtOH or glacial AcOH, a cryst. abietic acid, m. 161-5°, is obtained. Thus there is a series of acids differing in their contents of colloidal H_2O , from γ -pinic acid, the most highly hydrated, to abietic

acid, which is anhydrous. The possible range of sizing media is comprised between neutral Na abietate on the one hand and a colloidal hydrosol of abietic acid free from alkali on the other. The most coned. hydrosol, containing 0.61% of abietic acid, was obtained by adding an EtOH soln. of abietic acid to ice-cold H₂O, which had been freed from CO₂ by air, filtering the emulsion and concg. *in vacuo* below 50° until coarse flakes sep., then quickly filtering and cooling with ice. The behavior of various size fractions, has been studied by filtration, ultrafiltration, dialysis, diffusion, ultramicroscopy and electrophoresis. Dil. 1-5% solns. of neutral Na abietate pass through ultrafilters unchanged; they are diffusible and the state of dispersion is mol. At dilns. of 0.5% and below, hydrolysis takes place with opalescence due to sepn. of colloidal abietic acid. This has the properties of a suspensoid colloid and the commercial size emulsions are not emulsions but suspensions of abietic acid in mol. dispersed Na abietate. The colloid has a negative charge. As regards the relations of the viscosity of size solns. to temp., highly concd. solns. of Na abietate show the properties of a gelatinizable emulsoid colloid. In dil. solns. the viscosity of neutral Na abietate is relatively small and suspended colloidal abietic acid has no effect on viscosity. The chem. equil. in the hollander involves wide-reaching hydrolysis of the Na resinates and the Al₂(SO₄)₃. These hydrolyses are strongly influenced by the salts in the H₂O and by the free resin of the size. The H₂SO₄ liberated from the Al₂(SO₄)₃ neutralizes the peptizing action of the NaOH from the Na resinates. The flocculating action of electrolytes on abietic acid hydrosol has been studied quant. It is more powerful the greater the charge of the cation, while the peptizing influence increases with the charge of the anion. Thus mol. quantities of Al, Mg and K as chlorides required to produce incipient flocculation were in the ratio of 1:1700:5000, whereas in the form of SO₄ they were 1:50:150. The influence of Ca salts in the hollander H₂O is strongly flocculating; that of the Na salts is less but not inconsiderable. CO₂ has a weak flocculating action. Certain additions to commercial sizes act as protective colloids preserving the dispersion of the resin particles. The aq. ext. of casein is a powerful protective agent, but an alk. soln. of casein itself is flocculated by Al₂(SO₄)₃ and carries down the abietic acid by occlusion. Potato starch paste delays flocculation to some extent; small proportions of gelatin have a very powerful stabilizing action. These stabilizing colloids act similarly to mordants, preserving dispersion and constituting a bridge between the cellulose and the resin. Expts. by electrophoresis showed that pure paper pulp in H₂O migrates to the anode and consequently the pulp in the hollander carries a negative charge. If paper is ground up with coned. Al₂(SO₄)₃ soln. it then migrates to the cathode. Colloidal Al(OH)₃ carries a positive charge. Colloidal abietic acid carries a negative charge and behaves in exactly the same way as pure paper pulp. Thus fiber and colloidal resin are 2 similarly charged colloids which repel 1 another and a permanently sized paper cannot be made by pptg. the size with acid alone. Without the positive charge of the Al(OH)₃ the union between the fiber and the resin is due only to mechanical and capillary action. If too large an excess of Al₂(SO₄)₃ be used the charge of the whole system becomes positive and the quality of the sizing is impaired. Thus, according to the electrostatic theory of sizing, a firm, permanent sizing is only obtained when the condition is isoelectric, that is, when the positive charge of the Al(OH)₃ fixed in the pulp balances the negative charges of the paper and abietic acid.

C. J. WEST

New theories on rosin sizing. EMIL HEUSER. *Papierfabr.* 21, 289-94(1923).—See C. A. 17, 3100.

J. L. PARSONS

Water for sulfite mills. A. KLEIN. *Zellstoff u. Papier* 3, 103-4(1923).—A brief article concerning impurities in raw H₂O and their removal. In a mill making 30-35 kg. of bleached sulfite pulp per min. about 12,000 l. water were consumed. The distribution of this water was as follows: (1) 250 l. in the power plant, (2) 650 l. in the acid plant, including that for cooling the gases, (3) 300 l. in the cooking process, (4) 10,000 l. in the screening and washing operations, and (5) 300 l. in the bleaching baths and wet machines.

J. L. PARSONS

Sources of trouble in the coloring of paper stock and their elimination. H. DIERDORF. *Zellstoff u. Papier* 3, 105-9(1923).—Bleached ground wood should be entirely free from chemicals before it is colored; chem. residues often cause much trouble. In the selection of dyes for chem. wood pulps the degree of beating is of special importance. Basic colors have less affinity for bleached than for unbleached pulps. Each dye should be dissolved separately, preferably in hot H₂O, and not mixed before it is added to the beater. Some dyes do not dissolve readily in hard H₂O; distd. or condensed H₂O should be used. Filtering of the dye soln. is recommended, since ppts. often occur on standing.

J. L. PARSONS

Pulp and ground wood yields. B. POSSANER. *Zellstoff u. Papier* 3, 131-4(1923).—

The article is devoted almost entirely to the chemistry of the sulfite process. In the soda process the yield in straw pulp is about 40%, while with wood pulp it is only 35%. The sulfate process gives a yield of about 40%, and the sulfite process around 44%, based on the wood used. The following quantities of materials are required for 100 kg. sulfite pulp: 10-15 kg. S, 15-20 kg. CaCO₃, 100-140 kg. coal of which 30-40 kg. are for power, 40-60 for cooking, and 20-40 for drying the pulp. Approx. 1000 l. of cooking acid are required for 100 kg. pulp. The normal bleach loss is 8-10% of the unbleached pulp.

J. L. PARSONS

The microscopical differentiation of unbleached soda (sulfate) and sulfite pulps by Lofton and Merritt's method. G. WISBAR. *Mitt. Materialprüfungsamt* 6, (1922); *Wochbl. Papierfabr.* 54, 1993-6(1923); *Papierfabr.* 21, 349-51(1923).—The Lofton and Merritt test for unbleached sulfate and sulfite fibers in general proved satisfactory. With well cooked pulps the coloration was pale or entirely lacking. W. recommends the following modified procedure. A small sample of the fibrous suspension prepd. in the usual way is treated in a test-tube with a soln. prepd. as follows: 4.4 cc. of a 1% fuchsin soln. are added to 2.2 cc. of a 2% malachite green soln.; this is followed with 20 cc. of a 0.5% soln. of HCl, and the whole is dild. to 100 cc. with H₂O. The mixt. is boiled 1-2 min. The colors are somewhat different from those usually observed: the sulfite fibers are reddish violet, and the sulfate fibers are blue with a reddish or greenish tint. In comparing the American method with the German modification and with Klemm's test, in which rosaniline sulfate is used instead of fuchsin, the first mentioned gave higher results with sulfite fibers. Undecomposed particles of wood also are colored blue but can be distinguished from the sulfate fibers by their greater opacity.

J. L. PARSONS

The "Prodor" process for the manufacture of cellulose alcohol. G. VERNET. *Chimie et industrie Special No.*, 654-7(May 1923).—In this process (saccharification by means of cold 40% HCl satd. with HCl gas) the product must be cooled during absorption of HCl gas to prevent the temp. from rising above 20°, and must be heated during recovery of the HCl. The amt. of H₂O added (as HCl aq.) must be carefully controlled and the material must be spread in rather thin layers to prevent rolling into balls up to 15-20 cm. in diameter. The parts which come into contact with HCl are made of "Prodorite" a patented concrete (which can be reinforced) contg. no cement, which is absolutely resistant to all concns. of HCl up to about 120°. Saccharification is best carried out in an app. similar to a Herreshoff pyrites burner. A yield of about 250 l. of 100% EtOH per ton of dry sawdust is obtained. The residual lignin can be used as fuel or distd. for the production of MeOH, etc.

Manufacture of ethanol and methanol from wood. R. D. LANCE. *Chimie et industrie Special No.*, 638-41(May 1923).—L. suggests saccharifying wood for the production of EtOH and pyrogenating the residue for the production of MeOH, AcOH, etc., the charcoal being gasified and used for the pyrogenation. *Gymnospermus* are most suitable for this, and can also supply hydrocarbons for mixing with the EtOH and MeOH for use as fuel in Diesel engines.

The manufacture of ethyl alcohol from sulfite waste liquors. HARNIST. *Chimie et industrie Special No.*, 658-63(May 1923).—A description of the com. process with a brief discussion of possible improvements.

A. PAPINEAU-COUTURE

Lignin (GRÜSS) 10. Constitution of spruce-wood lignin (KLASON) 10.

Cellulose derivatives; treating textile fibers, yarns, and fabrics; dyeing textiles; paper. BURGESS, LEDWARD & Co., LTD. AND W. HARRISON. *Brit.* 192,173, Oct. 29, 1921. In consequence of the formation of cellulose derivs. contg. inorg. acid groupings, fibers or fabrics show an increased affinity for basic dyestuffs, and a resemblance to woolen fabrics. Wood-pulp or cotton so treated may be used for the manuf. of special qualities of paper where strength is required. Fibers, yarns, etc., are first treated with caustic alkali, and then either in the wet state or after drying, preferably at a temp. not exceeding 40°, are treated with inorg. acid chloride in the liquid or vapor form, but preferably dissolved in paraffin, gasoline, chlorinated hydrocarbons, etc. To obtain an increased luster, the yarn so treated may be subsequently mercerized, or the same effect may be obtained by applying tension in the case of yarn or pressure in the case of loose material, during the treatment with the acid chlorides. An increase of elasticity is obtained by subsequently treating the yarn or fabric with caustic alkali soln. of a strength above 6% without the application of tension or pressure; or alternatively, by employing in the first stage of the process a caustic alkali soln. above mercerizing strength and then treating with the acid chlorides without the application of tension.

Cellulose ester compositions. COLUMBIA GRAPHOPHONE CO., LTD., W. T. FORSG, F. W. JONES and G. WALTERS. Brit. 192,108, Aug. 25, 1921. A compn. suitable for the manuf. of gramophone records consists of cellulose acetate, gelatinizing agents such as sulfonamides, compd. ureas, anilides and their homologs, urethans, esters of oxamic acid, cyclohexanone, etc., and an acaroid resin in quantities preferably not exceeding the amt. of gelatinizer. Fillers, as carbon black, barytes, and kieselguhr, may be added. According to example, 2 parts of cellulose acetate, 1 part of acaroid resin, and 1 part of $p\text{-MeC}_6\text{H}_4\text{SO}_2\text{NHPh}$ are gelatinized on steam heated rolls. Three parts of carbon black are incorporated and the mass is molded into blocks which are reheated and molded, or the mass is allowed to cool and is ground into fine powder which is used to make the surface of laminated or other records. Volatile solvents may be added to assist in the gelatinization.

Cellulose ethers. P. C. SEEL. U. S. 1,464,158, Aug. 7. The exact amts. of cellulose, solid alkali, H_2O and EtCl or other etherifying agent necessary for production of a cellulose ether are sep. added to a reaction chamber and the materials are agitated and heated. The amt. of H_2O used does not exceed the amt. of the alkali by more than 25%. Cf. C. A. 17, 879.

Cellulose ether composition. S. J. CARROLL. U. S. 1,464,169, Aug. 7. A viscous, flowable, film-forming compn. is formed of cellulose ethyl ether dissolved in a mixt. contg. CHCl_3 and EtOAc , MeOAc or similar ester. U. S. 1,464,170 relates to similar compns. in which ethylene chloride may be used instead of CHCl_3 .

Recovery of sulfurous acid and heat from the waste gases from pulp boilers. H. CLEMM and C. HANGLER. Can. 233,150, July 31, 1923. The gases and vapors from pulp boilers are introduced without cooling into the raw lye in a closed tank under pressure.

"Self-copying" writing paper. A. G. E. LUNDGREN. U. S. 1,463,897, Aug. 7. One side of paper is treated with H_2SO_4 for parchmentization and is then coated with a coloring compn.

Sizing for paper. J. A. DECEW. U. S. 1,464,310, Aug. 7. A hot rosin soap is dild. in a cold soln. of an alk. cellulosic material, e. g., Irish moss, Iceland moss, linseed, viscose or regenerated cellulose.

Rendering paper translucent. A. KLIMENT. U. S. 1,464,477, Aug. 7. Paper or cardboard (which may have drawings on it) is treated with a mixt. of castor oil and oil of turpentine.

24—EXPLOSIVES AND EXPLOSIONS

CHAS. E. MUNROE

The importance of acid economy in the explosive industry. H. PAULING. Z. *angew. Chem.* 36, 71-2(1923).—Changing conditions in the manuf. of nitroglycerin are pointed out. At first the raw materials were $\text{C}_2\text{H}_5(\text{OH})_2$, HNO_3 and H_2SO_4 . Later plants made their own HNO_3 from Chili saltpeter and fresh H_2SO_4 , selling the denitrated spent H_2SO_4 and obtaining the by-product NaHSO_4 . Later still they coned. the denitrated H_2SO_4 for use with the Chili saltpeter. Next they made their own fuming H_2SO_4 which eliminated some of the H_2O from the HNO_3 employed. At present there is a lack of H_2SO_4 and improvements have made the concn. of HNO_3 to high strengths economical. The consumption of HNO_3 is now only that combined in the final product plus a small recovery and concn. loss, and of H_2SO_4 only the small concn. loss. The latter makes a complete cycle. There is no by-product. E. M. SYMMES

Density of mixed acids. PAUL PASCAL. *Mem. poudres* 20, 17-20(1923).—Dens. were made of the densities of H_2SO_4 from 90% to 100.5%, of HNO_3 from 73% to 98% and of 59 mixts. covering a wide range of compn. The dens. of each sample were made with a pycnometer at temps. from 3° to 35°, and d. was calcd. to 15° (referred to H_2O at 4°), a factor showing variation in d. per °C. being shown for each sample. Results obtained are tabulated and plotted graphically on a ternary diagram. The latter indicates that in the zone of mixts. used for the nitration of cotton, the d. is almost exactly a function of the H_2O content, a fact which may be of use in control laboratory work. C. G. S.

Applied blasting technic. D. KOHLER. Z. *Ges. Schiess-Sprengstoffw.* 18, 4-6 (1923).—Reviews the many applications of explosives in construction, demolition, agricultural, mining, and other industrial and engineering operations, and briefly describes methods of blasting. Lack of knowledge and proper training in the use of explosives

on the part of blasting overseers is the cause of a large proportion of the accidents occurring in the use of explosives.

C. G. STORM
Calorimetry of high explosives. R. ROBERTSON AND W. E. GARNER. *Proc. Roy. Soc.* 103A, 539-55(1923).—The calorimeter used was a V-steel bomb fitted with a special steel liner and an additional bottom plate which could be replaced when damaged by the fragments of the container fired within it and by the scoring from the detonation products. The free space in it was approx. 235-240 cc. Just before firing the pressure in it was reduced to a fraction of a mm. The charge of explosive, in pellets of 3.5-4.5 g. in wt., was confined in a steel cylinder with walls 0.25 in. thick, together with a vacuum-tight detonator. TNT, picric acid and 80/20 amatol in pellets of known densities were fired with fulminate or PbN_6 detonators. The heats of detonation found in cal./g. were for picric acid, with $Hg(ONC)_2$ detonators, 937, with PbN_6 , 912, for TNT, 926 and 926, resp. and for amatol, with PbN_6 only, 994. The total vols. of gases, in cc./g., were for picric acid with $Hg(ONC)_2$, 713, and with PbN_6 , 741; TNT, 716 and 703, resp., and for amatol, with PbN_6 only, 907. Each explosive had a density of 1.3. The permanent gases from TNT, when detonated with $Hg(ONC)_2$, consisted of CO_2 16.25, CO 48.2, CH_4 1.8, H_2 10.8 and N_2 23% but with PbN_6 it yielded less CO_2 and more CO and N_2 . The checkage on yields by the H content gave fairly concordant results. TNT yielded 46.5% of free C which reacts with the gaseous products to produce CH_4 and HCN . Owing to the reaction of the latter with the metallic fragments the amt. found depends on the rate of removal of the gases. In addition NH_3 , C_2H_2 and NO may be produced, depending on variations in conditions. The last named is formed in large quantity in a partial or slow detonation; an interesting table of gases produced when a gap intervened between a detonator and the charge of explosive is given, showing as much as 24% of NO present. Among the causes influencing the nature of the products are (a) density of loading in the container and in the bomb, (b) completeness of detonation and purity of explosive, (c) nature of the initiator, and (d) degree of tamping of the explosive. The gaseous reactions in cooling are mainly (1) $H_2 + CO \rightleftharpoons H_2O + C + 29.1$ cal., (2) $2CO \rightleftharpoons CO_2 + C + 39$ cal. and (3) $CO_2 + H_2 \rightleftharpoons CO + H_2O + 10$ cal. The formation of C is accompanied by an increase in the heat of detonation and a decrease in the vol. of gas liberated. The greater the density of loading and tamping of the explosive the higher the pressure through the cooling and the greater the deposition of C. For TNT the value for the ratio $[CO][H_2O]/[CO_2][H_2]$ varies from 4.8 to 5.6, which corresponds to a temp. of chilling of approx. 1850°.

CHARLES E. MUNROE
Oxygen-oil explosions. Preliminary report. I. M. D. HERSEY. *Bur. of Mines, Repts. of Investigations* No. 2507, 9 pp. (1923).—Because of the explosion in compressing O at the Jefferson Physical Laboratory of Harvard Univ., May 19, 1922, and the hazards in the repurification of He, an investigation has been undertaken to det. the limiting pressures and temps. above which compressed O and lubrication oils are capable of spontaneous explosion. The features of the problems involved are detailed, while lists of repts. of accidents, technical investigations and safety precautions are given. From expts. to date it is held that the critical temp. for explosibility of linseed oil under a pressure of 2500 lbs. per sq. in. of O appears to lie between 60° and 120°. C. E. M.

The use of explosives in checking large fires. *Tech. Division, Atlas Powder Co., Fire and Water Eng.* 74, 151, et seq.—After reviewing the use of explosives at the Boston, Chicago, San Francisco and other large conflagrations, the kind of explosives to be used and their methods of use are discussed and the precautions to be taken given. A policy for fire depts. is offered.

CHARLES E. MUNROE
The propagation of the explosion wave. P. LAFFITE. *Compt. rend.* 177, 178-80 (1923); cf. *C. A.* 17, 2958.—A glass tube 6 mm. in diam. was so fitted into a glass balloon, 18 cm. in diam., that the end of the tube just reached the center of the balloon. The system was fitted with $CS_2 + 2O_2$ mixt. which was ignited at the outer end of the tube by an elec. spark. A detonation wave, having a rate of 1800 m. per sec., was developed in the tube, which on reaching the contents of the balloon changed to a wave with a rate of 450 m. per sec. This produced a blow on the wall of the balloon which was repeated several times as it was reflected from the walls. When a detonator contg. 1 g. of $Hg(ONC)_2$, suspended in the center of the balloon, was detonated in the mixt. a rate of propagation of 1800 m. per sec. was secured in the balloon. C. E. MUNROE

Explosive tendencies of pulverized coal. HARTLAND SEYMOUR. *Chem. Age* (London) 9, 82-4.—A resumé of the reports of the U. S. Bur. of Mines (*C. A.* 16, 1506) with details of illustrative accidents.

CHARLES E. MUNROE
Gas explosions in furnaces and flues. V. KAMMERER. *Bull. soc. ind. Mulhouse* 89, 317-25(1923).—Discussion of their causes and methods of preventing them.

A. PAPINEAU-COUTURE

High-speed shadow cinematography and its application to the investigation of explosion phenomena and other very rapid reactions. CRANZ AND BAMES. *Z. angew. Chem.* 36, 76-80 (1923).—By specially arranged and ingenious spark illumination, carefully timed, it was possible to obtain pictures of refraction shadows whose time intervals of exposure were about one ten millionth of a second. Methods are described of avoiding the elec. lag of the transformer furnishing the illuminating spark. A series of illustrations is shown of the course of the flame formation from start to finish of the explosion of gas issuing from a Bunsen burner. Accuracy was checked by the Boudg e chronograph.
E. M. SYMMES

Explosive. W. B. STURGIS. U. S. 1,463,980, Aug. 7. Explosives which are powerful and have a low f. p. are formed of dinitrochlorohydrin, nitroglycerin, and nitrated sugar or other nitrated carbohydrate which does not solidify nitroglycerin. Tetranitrodiglycerin and nitrated HCl derivs. of diglycerin also may be used.

Explosives. DE WENDEL ET CIE, LES PETITS FILS DE F. Brit. 192,063, Jan. 11, 1923. Cork, wood, or like flour is added to combustible absorbents for liquid air to increase the proportion of absorbed liquid air available for combustion. Combustibles mentioned are C, hydrocarbons, sawdust, and metallic powders.

Explosive. W. O. SNEILING. U. S. 1,464,667, Aug. 14. Hydrous Ca borate to the amt. of 3-25% is incorporated with nitrate base explosives such as those used for coal mining in order to reduce the flame temp. Gypsum also may be used.

Explosives. W. FRIEDERICH. Brit. 192,830, Nov. 22, 1921. Basic Pb picrate, and other basic Pb salts of highly nitrated org. compds., for use in primers, percussion caps, and detonators are manufd. by adding a soln. of the nitro compd., preferably mixed with an alk. soln., to a Pb salt soln. while the latter is agitated, the addition being performed very gradually by drops. Mixts. of salts may be pptd. simultaneously. Besides basic Pb picrate, the following basic Pb salts are mentioned, namely those of trinitroresorcinol, di- and tri-nitroresorcinol, trinitroocresinol, hexanitrodioresorcinol, hexanitrodiphenylamine, di- and tri-nitrobenzoic acids, trinitrophenol, tetranitrophenol, di- and tri-nitroaminophenol, dinitrotrinitrobenzene, polynitrophenols, mono- and tri-nitromethane. Neutral salts such as the Pb salts of hexanitrophenylamine, and trinitroresorcinol may also be simultaneously pptd. with basic salts. Cf. 180,605, C. A. 16, 3399.

Propellant explosive. A. S. O'NEIL and R. R. EVANS. U. S. 1,464,012, Aug. 7. An intimate mixt. is formed of colloided nitrocellulose with a black powder paste contg. H₂O and alc., this mixt. is forced through a die and cut into granules.

Headless matches. S. HATAKEYAMA and C. FUNAI. Brit. 192,477, Nov. 1, 1921. Headless matches are made by impregnating splints by immersion in a boiling soln. of a fairly or easily sol. chlorate of an alkali or alk. earth metal, drying and then dipping the tips of the splints into a soln. of Ba(ClO₃)₂ and dextrin. The igniting ends may be colored. The impregnating soln. may contain 8 parts of KClO₃ to 100 of H₂O and the tipping soln. 2 g. of dextrin to 50 of Ba(ClO₃)₂ made into a satd. soln. Cf. C. A. 16, 3400; 17, 473.

25—DYES AND TEXTILE CHEMISTRY

L. A. OLNEY

Indigo dyeing in China. WOO DONG CHU. *Am. Dyestuff Rep.* 12, 579-82 (1923).
E. J. C.

The micro-sublimation of indigo. KARL PIRSCHLE. *Biochem. Z.* 136, 403-10 (1923).—Various indigo preps. were sublimed. With the 6-sided blue platelets of indigo blue were often found brown or reddish brown crystals of indigo red. When indigo-contg. plant material was sublimed directly, small crystals of indigo blue were sometimes obtained. The crystal forms are shown in figures. G. ERIC SIMPSON.

Influence of the temperature at which the solution of dyes is effected upon the nature of the solution. W. C. HOLMES. *Color Trade J.* 13, 54-6 (1923).—This investigation was undertaken in order to det. whether or not any regulation of temp. is necessary in the prepn. of dye solns. which are to be employed in spectrophotometric investigations. A table of spectrophotometric data is given for 6 dyes, which is in conformity with the corresponding modifications in the color of the solns. to the eye. Four types of behavior are found. The color change effected by heating solns. of erio violet 3R is extreme and is entirely irreversible. With solns. of diamine blue black, diamine black BO and diazine black DR concd., there occurs a decided modification in color with

increase in temp., and the restoration of the original color on cooling is incomplete. With diazo dark blue 3B the color is altered on heating but is completely restored on cooling. With pontamine violet N the color is not appreciably affected by heat, even temporarily. H. considers this change chem. and not colloidal in nature. Solns. of eric violet 3R prepd. with cold H₂O are heterogeneous and contain only relatively moderate amts. of true dye together with considerable amts. of 2 blue components which do not exhibit the complete nature of dyes, and which appear to be addition products. Under the influence of heating or org. solvents these addition products are completely transformed into true dye and the soln. is identical with pontamine violet N prepd. with hot or cold H₂O. The behavior of diamine blue black, diamine black BO and diazine black DR concd. may be explained by the presence of these addition products similar to those in eric violet 3R. The shade of paper dyed with eric violet 3R varies with the temp. of soln.

Fast green O and its related dyes. J. M. MATTHEWS. *Color Trade J.* 13, 42-5 (1923).—A review of the literature on fast green O as well as other dyes belonging to the nitroso or quinone oxime group. The structure, manuf., properties, reactions and uses are discussed.

Volumetric estimation of auramine. W. C. HOLMES. *Color Trade J.* 13, 45-8 (1923).—A method of estg. auramine is described wherein the auramine is pptd. quant. by an indigotin soln. with the formation of an insol. dye complex or lake, such as is usually formed by the interaction of an acid with a basic dyestuff. The soln. of auramine is titrated with an indigotin soln. of known strength, and the end point is detd. by the appearance of a blue coloration in a spot test upon filter paper. The results of a number of titrations are given. NaCl and dextrin do not interfere. The conversion factor of indigotin to auramine obtained by titration was 1.26, but theoretically it should be 1.3.

The estimation of erythrosin. WALTER HOLMES. *Color Trade J.* 13, 4-5 (1923).—Ppt. the color acid from 0.25 g. dye in 100 cc. H₂O with 5 cc. 0.6 N HNO₃, filter through a Gooch crucible, wash with 0.5% HNO₃ and finally with 10 cc. H₂O. Dry to const. wt. at 121° and calc. the wt. of dye by the conversion factor 1.074. C. E. MULLIN

The spectroscopy of dyes. W. C. HOLMES. *Color Trade J.* 13, 6-9 (1923).—Definite types of absorption are associated with definite types of chem. constitution, so that the analogy between the absorption of a compd. of unknown structure and that of related compds. of established constitution furnishes valuable evidence on the constitution of the former. It is probable that analogies in behavior under various influences, as established by quant. spectroscopic measurements, would provide equally valuable evidence of structure. The application of the spectroscope to dye identification is based primarily upon the correlation between constitution and color. The spectroscopic method affords a more positive identification of dyes than any other method, with the exception of some yellows and certain classes of dyes which do not give well defined absorption spectra, but it is not adapted to the direct detection and identification of minute amts. of dyes in the presence of large amts. of other dyes. The intensity, or magnitude, of the absorption of a dye soln. depends primarily upon the concn. of the soln., and with suitable regulation a relative estn., within 1 or 2%, of the dye content of a soln., in which the impurities are inert, may be made by a comparison of its absorption spectra with the spectra of a standard dye soln. However, the presence of secondary dyes often invalidates the spectrophotometric data as an index of practical color value, in much the same manner as in the TiCl₄ titration of dyes (cf. C. A. 17, 883). The most important application of the spectrophotometer for the dye mfr. will be found in the study of reactions, such as in plant control, etc. It will also be of service in detg. the nature of dye solns., the effect of concn., H-ion concn. and temp., and in studying the reactions of dyes in the formation of insol. lakes, dyeing, etc.

Sulfur dyes. R. F. HUNTER. *Chem. News* 127, 17-8 (1923).—Short descriptions are given for prepg. 13 of the commoner S dyes. The general method of procedure is to "dissolve crystals of Na₂S in water, add flowers of S, then the base, and boil under a reflux condenser until the desired stage is reached; filter, wash and dry. The process must be watched, since S dyes are complex condensation products, and if heating is carried too far, weird results appear." Blue and black dyes are usually derived from thiodiphenylamine, yellow and brown from thiazoles; immediate yellow is produced by fusion of dehydrothiolutidine with S.

The action of light on coloring matters. P. SISLEY. *Assoc. chim. industr. textile* 1922, 35-45 (Dec.); *Chimie et industrie* 10, 136 (1923).—A general discussion.

A. PAPIERAU-COUTURE

Blue dyestuff from furfural and diethylaniline. F. PASCHKE. *Cellulosechemie* 4, 32-3(1923).—PhNEt₂ and furfural were condensed by means of (CO₂H)₂ and the green product was heated under reflux with alc.-HCl, the brown soln. cooled and filtered, treated with NaCl, AcOH and FeCl₃. A blue dyestuff (A), C₂₂H₂₁N₃Cl₂O₁₀, sepd. as a black powder, purified by soln. in dil. AcOH, and repptn. with NaCl, and finally by dissolving in AcOH and evapg. to dryness. A in AcOH soln. dyes silk, and is a mordant dyestuff for cotton.

Vat dyeing by the Franklin process. D. R. KNEBLAND. *Textile Colorist* 45, 371 (1923).—General directions. LOUIS E. WISE
CHAS. E. MULLIN

An historical review of the steaming process in calico printing. J. R. HANNAY. *J. Soc. Dyers Colourists* 39, 169-75; *Am. Dyestuff Rep.* 12, 519-56(1923).—A brief history of the development as well as a description of the various types of modern steamers and their operation. CHAS. E. MULLIN

Dyeing astrachan fabrics. ANON. *Textile World* 64, 959, 1022(1923).—General directions. CHAS. E. MULLIN

Use of zinc dust in dyeing with synthetic indigo. BARRINGTON DE PUYSTER. *Color Trade J.* 13, 48-50(1923).—Instructions. CHAS. E. MULLIN

Blue dyeings with Griesheim naphthols and safranins. W. ZANKER and ERNST ZURLINDEN. *Textilchem. Col.* 1923, 101-5, 109-12. The claims made by the inventors for fastness of dyeings produced by a variety of methods from diazotized safranins and naphthols did not stand the test of commercial usage. Further, level dyeings with such products as Höchst Janus Dark Blue B and B.A.S.P. Indoin Blue BB are almost impossible of attainment. The Griesheim naphthols afford a base for level dyeings of high fastness on cotton, by coupling with diazotized Safranin T, etc. E. R. CLARK

The constituents of raw cotton. S. H. HIGGINS. *J. Soc. Dyers Colourists* 39, 150-1(1923).—In order that results may be comparative, a standard method of fiber extn. is necessary. The Soxhlet extn. of cotton with Et₂O for 35 hrs. is incomplete. Flax gave 1.39% wax by Et₂O extn. and on subsequent extn. with C₆H₆ a further 0.27%. C₆H₆ exts. the wax much more quickly than Et₂O on account of boiling at a temp. above the m. p. of the wax (cf. *C. A.* 17, 2195), although there is possibility of cellulose modification at high temps. Various solvents ext. different amts. of wax from the cotton, because of the complexity of the wax (cf. *C. A.* 17, 1890). EtOH exts. more from flax than C₆H₆, but the alc. extd. flax on extn. with C₆H₆ yields further material. It is immaterial if the alc. or C₆H₆ is used first, the extn. total is the same, but each solvent exts. different wax constituents. H. expresses doubt that Knecht and Street (*C. A.* 17, 2507), extd. all wax before the acid treatment. American cotton on extreme extn. with C₆H₆ gave 0.503% wax and on subsequent heating with dil. acid, a further 0.058%. Flax gave 1.65 and 0.16%, resp. K. and S. by the strong acid treatment caused degradation of the cellulose to lower compds. of an alcoholic nature or at least sol. in C₆H₆. An extn. of cellulose before and after powdering would be of interest. C. E. MULLIN

Chemical properties of cotton. II. Action of light. BARRINGTON DE PUYSTER. *Color Trade J.* 13, 23-6(1923).—A review. Very little has been published upon the action of light alone upon cotton, as most of the tests were made in the presence of moisture and air. Light and especially direct sunlight in the presence of air and moisture cause a yellowing with fiber deterioration in time. In the presence of metals or metallic salts, particularly Cu or Fe, the action appears to be accelerated, possibly catalytically. Diffused sunlight, yellow or red light rays appear to have very little action, while ultra-violet light causes a complete loss in tensile strength and the formation of oxycellulose. III. Action of water. J. M. MATTHEWS. *Ibid* 64-6.—A review. Hot or cold H₂O for short periods has comparatively no deleterious action on cotton. Cotton treated for 12 hrs. with boiling H₂O has an increased affinity for substantive, and a decreased affinity for basic, dyestuffs. When cotton is immersed in H₂O there is an evolution of heat, but as finely divided solids, such as silica and glass wool, also exhibit this exothermic action, it is not considered in the nature of a chem. reaction. Steaming under slight pressure for very short periods yellows cotton, possibly due to oxycellulose. Prolonged steaming materially weakens the fiber, but it is about 7 times as resistant as wool. Freezing does not appear to have any tendering action. CHAS. E. MULLIN

The regularity of yarns. A. E. OXLEY. *J. Soc. Dyers Colourists* 39, 175-8(1923).—An app. is described for recording photographically the regularity or evenness of twist in yarns. Tests show evidence of a periodicity of twist in mule yarns. Ring yarns show only non-periodic variations of twist due to differences in the roving. The longer draw of the mule tends somewhat to equalize roving variations. The yarn variations are sufficient in some instances to cause apparent faults in dyeing and finishing. CHAS. E. MULLIN

Action of heat on the chemical properties of cotton. J. M. MATTHEWS. *Color Trade J.* 12, 255-8(1923).—A review of the literature. Cotton loses 6-8% in wt. on heating to 100° and about 0.5% more on heating to 116°, all of which is regained upon exposure to moist air. On heating to 182° it has a further loss of about 1%, develops a yellow color and the fiber will not regain this final 1% loss. Structural disintegration begins at about 160° and at about 249° it gradually turns brown and its textile properties are destroyed. Much lower temps. for long periods have a similar deleterious action and various salts accelerate this action, possible catalytically. C. E. MULLIN

Technic of an Indian chintz. CYRIL G. E. BUNT. *Textile World* 63, 3489-91 (1923).—Some general information upon the production technic of the native prints. CHAS. E. MULLIN

The examination of fabrics by polarized light. P. KRÜGER. *Monatschr. Textilind.* 37, 227-8(1922); *Chimie et industrie* 10, 126(1923).—Differences in the various fibers are best brought out when the axes of the fibers are at 45° to the plane of polarization. A. PAPINEAU-COUTURE

Sizing materials for cotton fabrics. M. N. CONKLIN. *Color Trade J.* 13, 61-2 (1923).—A general discussion. CHAS. E. MULLIN

Para red colors on cotton goods. W. B. NANSON. *Textile Am.* 40, No. 1, 25, 29, 31-2; *Am. Dyestuff Rep.* 12, 583-4, 603-4(1923).—Detailed instructions for dyeing. C. E. MULLIN

The injury of fibers by washing. EBNER. *Z. angew. Chem.* 36, 323-6(1923).—A discussion of the various agents used for washing cotton goods is given with reference to their effect on the strength of the fiber. After 50 washings of 15 min. each with a 0.5% soln. of sodium perborate, the fibers lost 10% in strength. After washing with soap and soda, 50 washings of 5-10 min. duration with a weak NaOCl soln. were made. By this treatment the fibers lost 27% in strength. Further series of 50 washings were made with O₂ and with a washing agent contg. no available O. The former caused a loss of 40% in strength and the latter 60%. C. T. WHITE

Education and research in the textile industry. A. J. TURNER. *Am. Dyestuff Rep.* 12, 591-5(1923). E. J. C.

Cellulose derivatives; treating textile fibers, etc. (Brit. pat. 192,173) 23.

Dyes. SOC. ANON. FOUR L'IND. CHIM. À BÂLE. Brit. 191,854, Oct. 25, 1921. Triarylimethane dyes are obtained by condensing phenylchloroform or a substitution deriv. or homolog thereof, or 1-chloro-2-naphthylchloroform, with α -naphthol or a substitution product thereof having a free 4-position, in presence of a substance neutralizing acid; addition of a catalyst, for instance Cu or alc., is advantageous. The dyestuffs derived from 1-naphthol-2-carboxylic acid dye wool gray tints changed by after-chroming to green or blue tints fast to fulling and potting; they may also be dyed or printed on chrome-mordanted fabrics, or used in single-bath processes.

Dyes. SOC. ANON. POUR L'IND. CHIM. À BÂLE AND R. SALLMANN. Brit. 191,972, Feb. 8, 1922. Addn. to 104,045 (C. A. 11, 2046). The Cr compds. of azo dyes described in the principal patent and in 186,635 are prepd. by forming the parent dyestuffs in the presence of one of the chromating agents described in those specifications and heating the products until the dyestuffs are completely converted into their Cr compds.

Dyes. AET.-GES. FÜR ANILIN-FABRIKATION AND W. LANGE. Brit. 191,792, Oct. 10, 1921. Addn. to 16,592, 1915 (C. A. 11, 1553). The dyestuffs of the principal patent are modified by the replacement of the 4-acylamino-phenols by 2- or 3-acylamino-phenols substituted in the 4-position but having a free 2- or 6-position. According to an example diazotized picramic acid is coupled with 4-methyl-2-acetylamino-phenol. The products dye with chrome mordants olive shades of a more yellowish tint than those yielded by the dyestuffs of the principal patent.

Dyes. AET.-GES. FÜR ANILIN-FABRIKATION. Brit. 192,842, Nov. 28, 1921. Vat or pigment dyes are obtained by condensing a *p*-diazine in which the *p*-position to an azine N atom is substituted by a group contg. H capable of being replaced by metal, such as eurhodols or naphtho-sultamphenazines, with a 1,4-quinone or naphtho-sultam-quinone contg. halogen in the 2-position. The reaction is preferably effected in the presence of an agent which combines with HCl, such as AcONa, and an oxidizing agent, for instance by blowing in air or adding FeCl₃; when 2,3-dihalogen-1,4-quinones are employed an oxidizing agent is not required; when halogenated eurhodols are employed a metal such as Cu is added. Examples are given.

Vat dye. L. C. DANIELS. U. S. 1,464,598, Aug. 14. Dibenzanthrone 50 parts (free from impurities insol. in alk. hyposulfite soln.) is treated with HNO₃ (d. 1.46)

40 parts in the presence of PhNO_2 300 parts at a temp. of 50–60°, excess acid is neutralized with Na_2CO_3 , PhNO_2 is removed by steam distn. and the dye formed is recovered by filtration. It is a dark purplish powder.

Vat dye from dibenzanthrone. M. A. KUNZ. U. S. 1,464,070, Aug. 7. Dibenzanthrone is heated with H_2SO_4 and hydroxylamine sulfate (or hydrochloride) to obtain a dye which gives fast gray or black shades.

Azulmic acid dye. G. S. BOHART. U. S. 1,464,802, Aug. 14. A soln. of NaCN in H_2O is treated with slightly less than sufficient acid, e. g., H_2SO_4 , to decompose the cyanide, leaving still sufficient NaCN in the soln. to furnish the alk. condition necessary for causing the HCN liberated to change into azulmic acid. The azulmic acid which is formed is filtered and washed with H_2O . U. S. 1,464,803 relates to dyeing cotton or other material brown by treatment with an alk. soln. of azulmic acid followed by treatment with a dil. acid, e. g., a 1% soln. of HCl or HOAc. CuSO_4 may be used in acid soln. as a mordant as may also Co nitrate.

Dyes; intermediate products. ART. GES. FÜR ANILIN-FABRIKATION. Brit. 192,438, Sept. 27, 1921. *o*-Hydroxyazo dyes are prepd. by coupling a diazotized dihalo-2-aminophenol, contg. as a fifth substituent a halogen atom or an alkyl group, with a hydroxynaphthalenesulfonic acid or a substitution product thereof other than 8-halogen-1-hydroxynaphthalene-5-sulfonic acid. Examples of prepn. are given.

Intermediate products; dyes. L. B. HOLLIDAY & CO., LTD. AND G. T. MORGAN. Brit. 191,797, Oct. 12, 1921. Amino-1,2 naphtho-*p*-tolyltriazoles are obtained by coupling 5- or 8-nitro-2-naphthylamine with *p*-diazotoluene, oxidizing the nitro-2,1-amino-azo compd. to the corresponding nitrotriazole and reducing the nitro group.

Treating dyed yarns. A. ASHWORTH. Brit. 192,469, Nov. 1, 1921. To avoid the formation of Pb dust during the heading or shaking out and twisting of the dried hanks after the dyeing operation, the hanks are first subjected to hydroextraction, then to heading while in the moist state and then dried.

Finishing yarns and fabrics. A. G. BLOXAM. Brit. 192,227, Nov. 22, 1921. A linen-like effect is produced by subjecting cotton yarns of which the fineness does not exceed No. 80, and knitted and other fabrics made therefrom to cold mercerization in the manner set out in 108,671, *i. e.* with caustic alkali lye of over 20° Bé. and at a temp. below 0°. The goods may be treated before or after mercerization with H_2SO_4 of over 50.5° Bé. The acid may be cooled and the material may be stretched during the cold mercerization. The treatment with the cold lye may be conducted in the various ways described in 100,483, the treatments with the cold lye and with H_2SO_4 of over 50.5° Bé., cooled or not, being repeated once or several times. The cold mercerization may be combined with normal mercerization in the various ways described in 191,203. In all cases, the yarn or fabric may be subjected after treatment to one or more mechanical finishing operations such as calendering or mangling to increase the linen effect.

Artificial silk. E. BRONNERT. U. S. 1,464,805, Aug. 14. In the manif. of fine viscose threads by the stretch-spinning process, viscose of relatively thick consistency is caused to issue through relatively wide apertures into a coagulating soln. contg. a sol. aromatic sulfonic acid, e. g., PhHSO_3 and $\text{C}_6\text{H}_4(\text{HSO}_3)_2$, glucose and an ammonium salt, e. g., $(\text{NH}_4)_2\text{SO}_4$.

Artificial silk. E. BRONNERT. U. S. 1,463,793, Aug. 7. In manufacturing very fine threads from viscose, the rate of flow of the viscose from the forming nozzle and the concn. of the acid hardening bath are regulated in accordance with the thread diam. desired, the strength of the acid being increased according to the fineness of the threads by use of a soln. of acid contg. decomposed viscose. Cf. following pat.

Artificial silk; viscose. E. BRONNERT. Brit. 192,214, Nov. 14, 1921. In the manif. of very fine artificial silk threads from viscose according to the draw-spinning process described in 166,931 (C. A. 16, 501), to obtain highly lustrous threads, the individual filaments of which do not stick together, and to obviate the necessity for the careful adjustment of the degree of ripeness of the viscose, there is added to the highly coned. acid spinning baths employed, a soln. of cellulose, coagulated waste viscose, or coned. sulfite-cellulose lyes in 80% H_2SO_4 , the soln. being prepd. without heating; the soln. is dild. so as to give the required acid concn. in the bath. Cf. 21,405, 1907, 145,627, 147,416 and 181,900. Cf. preceding pat.

Viscose silk. E. BRONNERT. Can. 233,614, Aug. 21, 1923. In the spinning of very fine threads from viscose where the minimum concn. of H_2SO_4 is used with $(\text{NH}_4)_2\text{SO}_4$ in accordance with the desired fineness of the threads, part of the $(\text{NH}_4)_2\text{SO}_4$ is replaced by Na_2SO_4 . Relatively large apertures are used in spinning. Cf. C. A. 16, 1018.

Proofing fibrous materials. V. SCHOLZ. Brit. 192,387, Jan. 23, 1923. Fibrous

materials are immersed alternately in a neutralized soln. of bark-tanned leather in alkali and an aq. soln. of a substance which will ppt. the leather upon the fibers. The neutralization may be effected by means of dil. acids, CO_2 , fatty acids, fats, oils, resins, "cell-pitch," etc. Salts of Al, Fe, Cu and Ca are mentioned as being suitable precipitants; also org. salts, acids and bases. The usual coating of paint on the fabric backing of linoleum may be dispensed with by treating the fabric by the above process.

Treating wool fibers for spinning, etc. BRITISH OIL PRODUCTS CO., LTD., AND H. W. HURRON. Brit. 192,105, May 18, 1922. Wool fibers are treated for spinning, etc., with a water-sol. oil prepd. by (a) sulfonating 1 part of castor oil with $\frac{1}{4}$ its wt. of vitriol at 90°F ., the product being washed after 24 hrs., sepd., and neutralized with NaOH; (b) sulfonating 1.5 parts of a fatty oil other than castor oil under similar conditions, adding thereto 2-4 parts of a non-sulfonated fatty oil, and then washing and sepg. the product; (c) mixing the products obtained in (2) and (b) and neutralizing the whole with NaOH.

Treating cotton, linen, jute and hemp. R. C. WILD. Brit. 191,800, Oct. 13, 1921. To remove pectic matter and to increase the absorptive capacity, cotton, linen, jute, or hemp is boiled in an alk. soln. to remove part of the impurities; washed in H_2O , then boiled in H_2SO_4 soln. and finally washed. 100 kg. of cotton piece goods, such as heavy shirtings, are boiled in 600 l. of an aq. soln. contg. 2.4 kg. of NaOH and 1 kg. of Castile soap for 3 hr., then washed and boiled in 600 l. of H_2O contg. 2.94 kg. of H_2SO_4 (d. 1.841) for 1.5 hrs. and finally washed. Egyptian cotton, duck, linen, hemp or jute is similarly treated but requires a stronger soln. of NaOH, or preferably longer boiling, say 4 hrs. in the NaOH soln. and 2 hrs. in the acid soln. Cotton yarn in hank form could be similarly treated but this requires only 2 hrs. in the NaOH soln. and 1 hr. in the acid soln. The NaOH may be replaced by KOH, Na_2CO_3 or K_2CO_3 , and the Castile soap may be replaced by ordinary soap other than resin soap. H_2SO_4 may be replaced by HCl.

26—PAINTS, VARNISHES AND RESINS

A. H. SABIN

Driers. ANON. *Farb. u. Lack* 1922, 275, 284, 291, 301(Aug. 17, 24, 31, Sept. 7); *Chimie et industrie* 10, 126(1923).—A review of the prepn. of driers. A. P.-C.

Treatment of hard resins to increase their solubility. G. H. SMITH. *Farb. u. Lack* 1922, 283, 293, 299(Aug. 24, 31, Sept. 7); *Chimie et industrie* 10, 126(1923).—Review of some German patents. A. PAPINEAU-COUTURE

The lacquering of sheet metal. ANON. *Farb. u. Lack* 1922, 308(Sept. 14); *Chimie et industrie* 10, 126(1923).—Brief review of methods used. A. PAPINEAU-COUTURE

Linseed oil. P. TORELLI. *Boll. chim. farm.* 62, 323-4(1923).—Adulteration of linseed oil may be detected by adding 8 cc. of a 2.5% soln. of AgNO_3 in 99% EtOH to 20 cc. of the oil and immersing the container in boiling H_2O for 10 min. The development of color indicates adulteration as follows: black, cottonseed; dirty green, colza; red, sesame; yellowish green, poppy seed. When pure linseed oil (6 cc.) is treated with 2 cc. of concd. H_2SO_4 , a brownish red, then a black color forms. Other colors indicate adulteration as follows: reddish yellow, cottonseed; brownish yellow, colza; brownish orange, sesame; yellow, poppy seed; violet, resin. A. W. DOX

Insulating varnishes (WEBER) 4.

Metallic paints. J. A. RITCHIE. Brit. 192,772, Nov. 8, 1921. A powder from which a metallic paint is made by the addn. of H_2O consists of finely divided dextrin and a metallic powder such as bronze powder and 1-2 parts of dextrin are used. The powder may be moistened and pressed into cakes.

Pigments. D. WHYTE. Brit. 191,886, Nov. 11, 1921. PbSO_4 water paste is converted into oil paste for use in paint manuf., by initially drying the water paste, e. g., in hydro-extractors, drying-chambers, etc., to remove free H_2O , and then churning it with sufficient oil to destroy the cryst. structure and set free the H_2O of crystn. In an example, 9% of oil is used.

Tung-oil paint and varnish mixture. H. A. GARDNER. U. S. 1,463,883, Aug. 7. Tung oil is combined with a dechlorinated oil such as the product obtained by chlorination and subsequent dechlorination of a paraffin type hydrocarbon oil. U. S. 1,463,884 relates to the use of a similar compn. for impregnating or coating wood, paper, concrete, metal walls of tanks or similar materials, e. g., for forming laminated solid articles.

Varnish, paint and waterproofing composition. P. M. STEWART. U. S. 1,464,224, Aug. 7. A compn. adapted for use on various materials is prepd. by adding an unsatd. vegetable oil such as China wood oil to P_2O_5 , and then adding linseed oil and "Cumar" or rosin. The linseed oil and "Cumar" are mixed and heated together before incorporation with the other ingredients.

Polymerization resin from naphtha. S. P. MILLER and J. B. HILL. U. S. 1,464,151, Aug. 14. See Can. 217,322 (C. A. 16, 1875).

Ink. H. KRUSE and W. C. KRUSE. U. S. 1,464,044, Aug. 14. An ink which is suitable for mimeographing is formed of Turkey red oil, saponified resin varnish, C black and malori blue.

27—FATS, FATTY OILS, WAXES AND SOAPS

E. SCHERUBEL

Hydrogenation of fats. I. Effect of some substances upon the nickel catalyzer. S. KITA and T. MAZUME. *Z. angew. Chem.* 36, 389-91(1923).—See C. A. 17, 2368. E. J. C.

Chemical studies of pombi. J. PIERRAERTS. *Bull. agr. Congo Belge* 14, 201-3 (1923).—Chem. analyses are given of the shell, nut and pressed cake of pombi. The analyses indicate that the nut may be of value as source of oil and also as feed for live stock. M. S. ANDERSON

Preparation of palm oil on the West African coast. PAUL AMMANN. *Chimie et Industrie Special No.*, 775-7(May 1923).—The extn. process used by the natives is described. Its main faults are the excessive amt. of labor required and the fermentation which is allowed to proceed so as to soften the fruit so that it can be more easily worked. This results in high acidity (15-50% as oleic). By treating the fruit immediately after picking an edible oil can be obtained directly with very low acidity (not over 1.5%). A. PAPISEAU-COUTURE

The occurrence of zinc in oils from animals and plants (WOLFF) 11A. Apparatus for feeding sulfur dioxide (U. S. pat. 1,463,818) 1.

Refining animal fats. J. W. RUWE. U. S. 1,464,627, Aug. 14. Tallow stock or similar animal fat is mixed with a vegetable oil, e. g., cottonseed or peanut oil, and the mixt. is heated to below the temp. at which the animal fat alone would melt. NaOH soln. is added to combine with free fatty acids present but not to saponify the neutral fat, the mixt. is allowed to stand until the neutral fat and soap stock stratify and the ayes which form are sepd.

Washing powder. H. J. HAYWARD. Brit. 192,232, Nov. 25, 1921. Four lbs. of Castile soap is boiled in 2 gal. of H_2O , and 10 lbs. of Na_2CO_3 is added together with 1 oz. of NaOH (95%) in just enough H_2O to dissolve it. The mixt. is dried and crushed to powder.

28—SUGAR, STARCH AND GUMS

F. W. ZERBAN

Report on the meetings of the Association of Technical Advisers of the Java Sugar Industry. I. Joint meeting. ANON. *Arch. Suikerind.* 31, Part 4, 1-57(1923).—A round table discussion on the following subjects: deterioration of cut cane, cane weighing, detn. of degree of maturity, estn. of the yield obtainable from certain fields, and the effect of cane variety on mfg. operations. F. W. ZERBAN

The evaluation of raw sugar: redemption or refinery value? GUSTAV GLASER. *Z. Zuckerind. czechoslov. Rep.* 47, 495-6(1923).—If P is the polarization, N the non-sugar content, and W the moisture of the raw sugar; and p the polarization, n the non-sugar, β the Brix, and Q the purity of the molasses, the actual yield of refined sugar is the "refinery value" and is given by $R = P - Q[100 - (P + W)] / (100 - Q)$. This is shown to give a better basis for evaluation than the usual redemption. W. L. BADGER

Sterilization of sugar solutions by Filter-Cel. ROBERT CALVERT and ALFRED NIGHT. *Facts About Sugar* 17, 178(1923).—Previous work is reviewed. It is demonstrated by expt. that the filtration of raw sugar solns. with Filter-Cel is very effective in removing microorganisms. Fermentation tubes were made up from the filtered liq.

uors and incubated at 40°; practically no fermentation resulted in any case.

T. S. HARDING

Calculation of mill extraction. E. HADDON. *Rev. agr. Maurice* 1, No. 9, 110-5 (1923).—Assuming cane contg. 87% juice, 10% dry fiber, a recovery of 60% of the juice in the first 2 mills, and a moisture content of 46.1% in the bagasse, the extn. will be 90.2% without maceration, 95.3% with 20% maceration, and 96.3% with 30% maceration. With 80.5% juice and 15% dry fiber the extn. will be 82.9, 92.6, and 94.1%, resp. Deerr's figures are given for comparison.

F. W. ZERBAN

Cane juice and its purification. L. GIRAUD. *Rev. agr. Maurice* 1, No. 9, 115-8 (1923).—A general discussion of known data and methods.

F. W. ZERBAN

Determining the decolorizing power of bone black in sugar houses. R. GILLET. *Boll. assoc. ital. industr. zucchero* 15, 117-21(1922); *Chimie et industrie* 10, 146(1923).—Prep. a standard molasses soln. (free from invert sugar) having a color value of 30 "colories" (3.3 divisions on the Stammer colorimeter) by dilg. with a suitable amt. of water. Wash the bone black 3 times at 10 min. intervals with a suitable amt. of boiling water, dry at 120-130° for 3 hrs. To 100 g. of bone black in a 500-cc. Erlenmeyer flask add 250 cc. of the standard molasses soln., boil under an air reflux condenser (1.2 m. long) for 5 min., shaking at 1 min. intervals, let cool 3 min., filter through paper, passing the first portions through repeatedly until clear, and compare in a Stammer colorimeter with a blank run without bone black. The difference between the 2 readings gives the decolorizing value, which should be about 85-95%.

A. P.-C.

The action of decolorizing blacks in the sugar industry. R. GILLET. *Boll. assoc. ital. industr. zucchero* 15, 121-4(1922); *Chimie et industrie* 10, 146(1923).—Differences in the decolorizing power of bone black with various juices are attributed to differences in the nature of the coloring matters.

A. PAPINEAU-COUTURE

Clarifying starchy liquids. A. GUSMER. *Brit.* 191,888, Nov. 12, 1921. See U. S. 1,406,554 (C. A. 16, 1626).

29—LEATHER AND GLUE

ALLEN ROGERS

Solved problems of tanning. LEOPOLD POLLAK. *Gerber* 49, 49-51, 57-60, 67-9, 73-5(1923).—A review.

H. B. MERRILL

Second report of the French Committee on Leather Analysis. PAUL CHAMBARD. *Cuir* 12, 332-5(1923).—The official methods for the detn. of moisture and H₂O-sol. matter are discussed, and results obtained by different analysts are given. The method for detg. free H₂SO₄, proposed by Jalade (C. A. 17, 1731), is discussed.

H. B. M.

Report of the French Committee on Tannin Analysis. G. HUGONIN. *Cuir* 12, 328-31(1923).—Details of the French official method are given, together with analytical results obtained by the method of 6 different analysts. The necessity for specifying the type of grinding mill employed, and the type of extn. app. and no. of washings is pointed out. Also in *J. Soc. Leather Trade Chemists* 7, 318-27(1923).

H. B. MERRILL

Modern technology of automobile leather production. A. G. WIKOFF. *Chem. Mel. Eng.* 29, 309-13(1923).—A description of the processes of the General Leather Co., with 13 illustrations. A special feature is a method of setting out leather for drying which obviates the necessity for tacking and gives a substantial increase in area.

J. A. WILSON

The concentration factor in the combination of tannin with hide substance. A. W. THOMAS AND MARGARET W. KELLY. *Ind. Eng. Chem.* 15, 928(1923); cf. C. A. 16, 1678.—Points of max. were found in all curves showing the rate of combination of tannin with hide substance as a function of concn. of exts. of wattle, hemlock, larch, and oak barks. At all points up to the max. in each case, the solns. were completely detannized by the hide powder, but where more tannin was present than could be fixed by the hide, the curves slope steeply downward. Theoretical aspects are discussed.

J. A. W.

Notes on some tanning barks of Madagascar. HEIM AND M. CERCELET. *Cuir* 12, 324-5(1923).—Analyses of six barks are given, with a discussion of their possible utilization for tanning.

H. B. MERRILL

The manufacture of tanning extracts. R. SANSONE. *Rev. chim. ind.* 32, 89-91, 199-204(1923).—A description of the com. process.

A. PAPINEAU-COUTURE

Glues and adhesives and their applications. MAURICE DE KEGHEL. *Rev. chim. ind.* 32, 120-3, 147-50, 170-8, 191-3(1923).—A review.

A. PAPINEAU-COUTURE

